L Number	Hits	Search Text	DB	Time stamp
1	140	capillary adj tube with droplet	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2004/01/08 07:10
2	53	capillary adj tube with droplet and pump	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2004/01/08 07:31
3	1889	well with droplet	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2004/01/08 07:49
4	2	wellplate with droplet	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2004/01/08 07:55
5	20	well with (droplet adj generator)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2004/01/08 07:50
6	55	(well adj plate) with droplet	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2004/01/08 07:56
7	1	(well adj plate) with droplet and (drop adj generator)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2004/01/08 07:57

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United States Patent [19]

Chun et al.

[11] Patent Number: **5,266,098**

[45] Date of Patent: **Nov. 30, 1993**

[54] **PRODUCTION OF CHARGED UNIFORMLY SIZED METAL DROPLETS**

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[73] Assignee: **Massachusettes Institute of Technology**, Cambridge, Mass.

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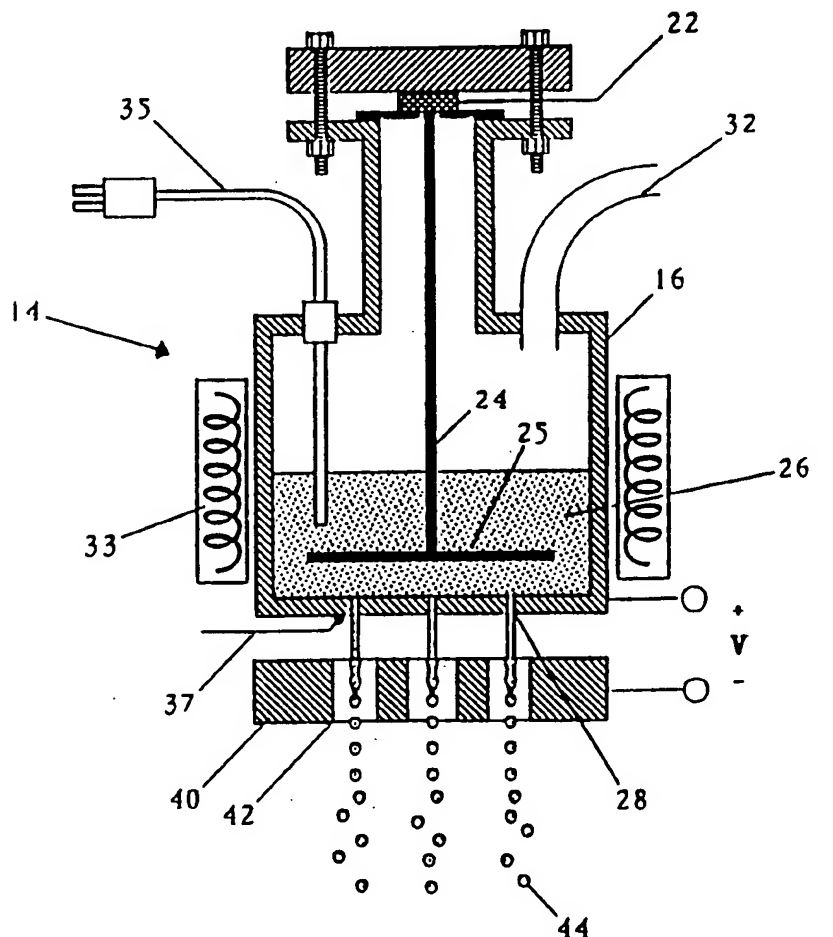### FOREIGN PATENT DOCUMENTS

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Primary Examiner—George Wyszomierski
Attorney, Agent, or Firm—Robert F. O'Connell

[57] **ABSTRACT**

A process for producing charged uniformly sized metal droplets in which a quantity of metal is placed in a container and liquified, the container having a plurality of orifices to permit passage of the liquified metal therethrough. The liquified metal is vibrated in the container. The vibrating liquified metal is forced through the orifices, the vibration causing the liquified metal to form uniformly sized metal droplets. A charge is placed on the liquified metal either when it is in the container or after the liquified metal exits the container, the charging thereof causing the droplets to maintain their uniform size. The uniformly sized droplets can be used to coat a substrate with the liquified metal.
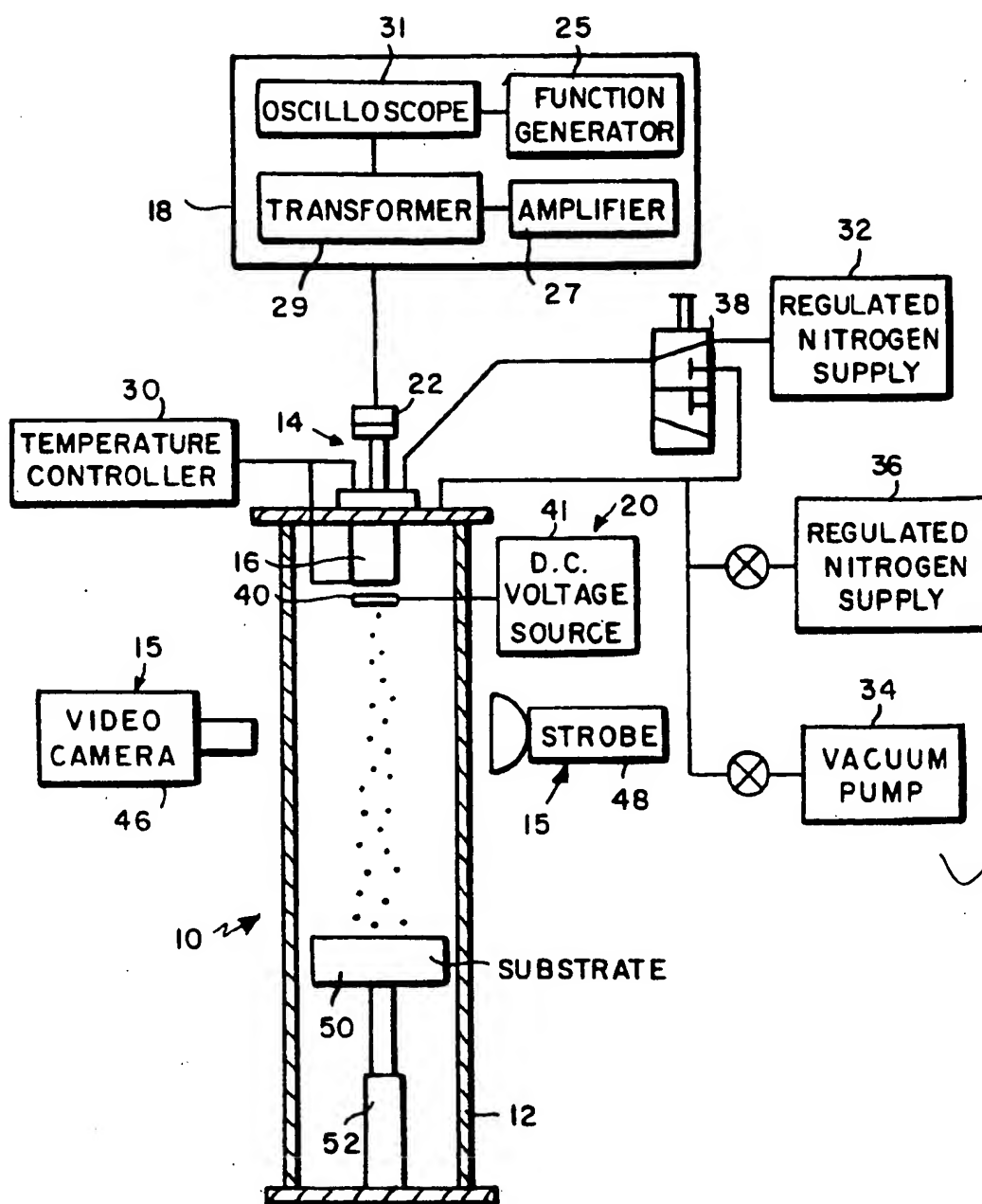
19 Claims, 3 Drawing Sheets

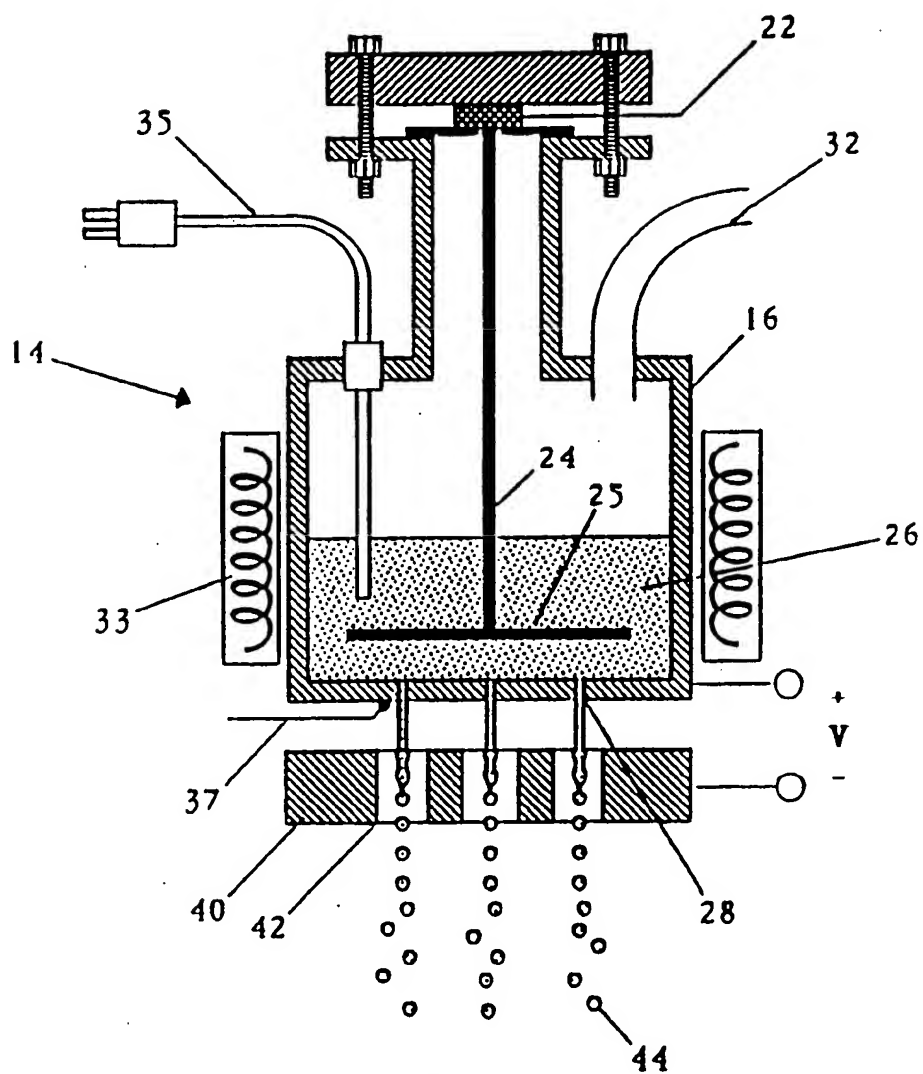OSCILLOSCOPE   FUNCTION GENERATOR

TRANSFORMER   AMPLIFIER

REGULATED NITROGEN SUPPLY

TEMPERATURE CONTROLLER

D.C. VOLTAGE SOURCE

REGULATED NITROGEN SUPPLY

VIDEO CAMERA

STROBE

VACUUM PUMP

SUBSTRATE

FIG. 1

Figure 2

Figure 3

PRODUCTION OF CHARGED UNIFORMLY SIZED METAL DROPLETS

BACKGROUND OF THE INVENTION

The production of metal droplets is useful in a variety of research and commercial applications. Such applications include metal powder production, rapid solidification research, spray forming of discrete parts, spray forming of strips, spray forming of metal-matrix composites and metal coating. In carrying-out these applications, there are a variety of methods used to produce the metal droplets such as atomization of molten metal by gas jets or by high pressure water, spraying molten metal onto a spinning disc (melt spinning) or into a vacuum to form discrete particles, vaporization of metal in a vacuum followed by condensation, fusion of metal in a vacuum followed by condensation, fusion of metal by an electric arc followed by the formation of droplets which are forced out of the arc zone, and forming a molten surface on a metal rod and agitating the metal at an ultrasonic frequency.

Another technique to generate metal droplets, particularly for research purposes, is electrohydrodynamic (EHD) spraying. The EHD technique comprises the use of a very intense electric field at the tip of a capillary tube through which molten metal flows. The electrostatic stresses applied by the electric field at the tip of the small capillary tube result in a highly dynamic process at the charged liquid surface, resulting in charged droplet formation. EHD processes and variations thereto are disclosed in U.S. Pat. No. 4,264,641 and "Application of Electrohydrodynamic to Rapid Solidification of Fine Atomized Droplets and Splats," Perel et al, Mar. 23-26, 1980, at the Conference on Rapid Solidification Processing, Principles and Technologies, II, Reston Va.

While each of these known processes have their advantages and have achieved varying degrees of success, none of them is capable of producing with any consistency metal droplets uniform in size, shape, initial velocity, and thermal state.

Ink jet printing processes, while producing uniform liquid droplets, are not concerned with producing charged uniformly sized metal droplets. Also, maintaining a separation between droplets is not a problem or an issue in ink jet printing because the distance from the ink nozzle to the printing surface (paper) is no more than a few centimeters. This is unlike metal droplet processes wherein the distance from droplet formation to the substrate or collector needs to be sufficiently extended for the metal droplets to cool and at least partially solidify. As such the distance generally must be at least about 25 centimeters. At such a distance, droplets in a stream broken from a jet would naturally merge with one another, with the merging destroying any uniformity of initial droplet distribution.

Accordingly, it is an object of the present invention to develop an apparatus and process for producing charged uniformly sized metal droplets. By virtue of the charge, droplets are prevented from merging in flight and thus they can remain uniformly sized until they solidify or are collected on a substrate. Furthermore, the charge on the droplets makes it possible to manipulate the flight of the droplets with externally applied electric fields.

It is another object of the present invention to produce charged uniformly sized metal droplets for use in research and commercial applications.

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a process and apparatus for producing and maintaining charged, uniformly sized metal droplets and to the charged uniformly sized metal droplets themselves. As used herein "maintaining" means that the droplets once formed remain uniformly sized until they either solidify or are collected on a substrate.

The process of the present invention requires the use of an apparatus comprising a spray chamber and a droplet generator disposed within the spray chamber for producing charged uniformly sized metal droplets and preferably a monitoring system for monitoring and controlling the droplet formation process. The droplet generator generally comprises a container for holding and liquefying a charge of metal, a forming means for forming uniformly sized metal droplets, and a charging means for charging the metal droplets. The forming means is preferably either a vibrating means for vibrating the molten metal in the container or at least one oscillating gas jet disposed outside the container at the point where the liquefied metal exits the container.

The process generally comprises liquefying metal in the droplet generator container which has at least one droplet-forming spray orifice, charging the liquefied metal, and forcing the liquefied metal through the at least one orifice and thereafter forming charged uniformly sized liquid metal droplets which maintain their uniform size.

In one embodiment the liquefied metal is formed into uniformly sized metal droplets by vibrating the liquid metal while it is in the container and forcing it out of an orifice in the container so as to form metal droplets. As the liquefied metal exits the at least one orifice as a jet, the imposed vibrations in the liquefied metal cause it to break up into uniformly sized metal droplets. In an alternative embodiment at least one oscillating gas jet is positioned at the exit point of the liquefied metal from the container to create the uniformly sized metal droplets.

In both of these embodiments, the metal droplets may be charged by either charging the liquefied metal while it is in the container or by charging the droplets as or after they are formed after exiting the container.

After the metal droplets are formed, they continue their descent through the spray chamber to a collecting means such as a substrate. The end use application of the metal droplets will, of course, determine the composition of the droplets and the substrate. The substrate may include a powder collection container, a metal or ceramic plate for producing deposits, a half-mold for producing shapes, a roller for producing sheets, a wire, a part to be coated, and a metal sheet.

The metal droplets formed using the process and apparatus of the present invention are in each case of uniform size and shape; i.e. they are substantially spherical in shape and have diameters which vary in degree by no more than about $\pm 25\%$, preferably by no more than about $\pm 10\%$, still more preferably by no more than about $\pm 5\%$, still more preferably by no more than about $\pm 3\%$, and most preferably by no more than

about ±1%. The metal droplets are formed having this uniformity without the need for any size classification procedures. As used herein "metal droplets" includes both liquid and solid metal droplets. The process of the present invention is capable of producing metal droplets having diameters which may be controlled to be within the range of from about 10 to 500 micro-meters (µm), depending upon the specific process conditions employed.

The process and apparatus of the present invention are useful in numerous end use applications including uniform powder production, rapid solidification research, spray forming of discrete parts, spray forming of strips, spray forming of metal matrix composites, and metal coating.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of the first embodiment of the metal droplet formation apparatus of this invention.

FIG. 2 is a cross-sectional view of the metal droplet generator of the apparatus of FIG. 1.

FIG. 3 is a cross-sectional view of the second embodiment of the metal droplet formation apparatus of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings, the process and apparatus for use in carrying out the process will now be described.

As shown in FIG. 1, a droplet formation apparatus 10 generally comprises a spray chamber 12, a droplet generator 14, and a monitoring system 15. As best shown in FIG. 2, the droplet generator 14 generally comprises a container 16, a vibrating means shown generally as member 18, and a charging system 20. The vibrating means 18 comprises a function generator 25, an amplifier 27, a transformer 29, an oscilloscope 31, and a piezo-electric transducer 22, such as a lead metaniobate piezo-electric transducer, connected to a shaft 24 and disk 25 which extends into container 16 and into a liquefied metal 26. The vibrating means produces small, regular oscillations through the orifices 28 that break the jet of liquefied metal being forced through the orifices into uniform metal droplets as the metal jets exit the orifices. The metal droplets then pass through a charging plate 40 with a suitable opening for each jet or set of jets. The charging plate 40 is positioned at about the point where the jets of metal break into individual droplets. The function generator, amplifier, and transformer drive the piezo with up to about 300 volts at about 1 to 100 kHz. At this voltage, a 3.2 mm thick lead metaniobate piezo transducer vibrates with an amplitude of about 0.1 µm. Any piezo transducer which will produce vibrations of a similar magnitude may be used. The vibrations are transmitted down the shaft 24 through the disk 25 and into the liquefied metal 26. The shaft protects the piezo from the heat of the liquefied metal 26 and the vibrations transmitted through the liquefied metal cause the metal jets to break into uniform droplets as they exit the spray orifices 28. In order for the piezo to operate it must be maintained sufficiently below its Curie temperature so that it does not de-pole and lose its piezo-electric characteristics that enable it to vibrate. The length of the shaft therefore depends upon the temperature of the molten metal in the container and on the Curie temperature of the piezo-electric crystal. Typically, the

shaft will extend about 10 cm above the molten metal. In an alternative embodiment (not shown) the piezo transducer based vibrating means may be replaced by an electro-mechanical agitator.

The container 16 is constructed of a suitable material for holding molten metal such as, for example, a higher melting point metal like stainless steel or a ceramic such as fused silica, graphite, or alumina. The container is provided with an air tight seal (not shown) at its top such as a knife edge rim against a soft copper gasket. The bottom of the container 16 has at least one, but preferably a plurality of orifices 28 through which liquefied metal 26 is forced as jets. While any suitable material may be used to form the orifices 28, they are preferably drilled in sapphire or ruby jewels such as those supplied by Bird Precision of Waltham MA. Preferably, they have length to diameter ratios of about one, polished inner diameters, and sharp, burr-free edges. The orifice jewels are mounted in pockets on the bottom of the container, preferably with a high temperature ceramic adhesive. Depending upon the end use of the metal droplets, the orifice sizes and number of orifices may be varied. For example, for spray characterization experiments only a single orifice need be used. For spraying deposits, a grid orifice having up to about 100 individual orifices can be used to create high mass fluxes. Orifice diameters may range from about 25 to 250 µm. An orifice with a diameter of 50 µm can produce droplets having diameters of from about 80 to 110 µm. An orifice with a diameter of 75 µm produces droplets having diameters of from about 120 to 165 µm. An orifice with a diameter of 100 µm produces droplets with diameters of from about 160 to 220 µm. The exact size of the droplets produced is a function of the jet diameter (d), the jet velocity (V), and the frequency of the imposed vibrations (f). The jet diameter (D) is determined primarily by the orifice diameter but also is a function of the jet velocity. The general relationship among these parameters is:

$$D = \sqrt[3]{\frac{3\,d^2\,V}{2f}}$$

Associated with the container 16 is a temperature control system 30 which includes a heating means 33 for melting the metal 26 within the container 16. While any suitable temperature control system may be employed, as shown in FIG. 2, it is presently preferred to employ a system comprising two 300 watt resistance band heaters, two thermocouples 35 and 37 (one in the melt 26 and one at an orifice 28), a digital temperature controller (not shown) and a temperature display (not shown).

Associated with both the droplet generator 14 and the spray chamber 12 is a pressure and atmospheric control system. As best shown in FIG. 1, the pressure control system controls the atmosphere in the spray chamber 12 and forces liquefied metal from the container 16 through the orifices 28. The system comprises two regulated gas supplies 32 and 36, a vacuum pump 34 and a three-way valve 38 that connects the container 16 to either the spray chamber 12 or one of the pressure sources 32. The other pressure source 36 and the vacuum pump 34 are connected directly to the spray chamber 12. The presence of oxygen in the spray chamber hinders and may prevent the formation of the metal droplets. Accordingly, the atmosphere within the spray chamber and the container is substantially oxygen-free.

To accomplish this, the apparatus is evacuated and flushed with an inert gas such as nitrogen, argon, or helium before being operated. The inert gas atmosphere is maintained during use.

A pressure differential across the orifices 28 between the container and spray chamber of at least about 5 psi is required to form a jet of liquefied metal. A pressure differential of between about 20 and 100 psi is preferred. To avoid producing a jet prematurely, container 16 is connected to the spray chamber 12 during the oxygen evacuation and flushing procedure prior to use. This equilibrates the pressure in the spray chamber and the container 16. Then, to create a liquid jet, the three-way valve 38 is turned to the pressure source 32 to produce the desired pressure differential needed to produce a liquid jet.

The droplet charging system 20 generally comprises a charging plate 40 having holes 42 which are aligned with the orifices 28 to permit the flow of metal droplets 44 therethrough and a voltage source 41. The plate 40 is preferably made of a highly conductive metal such as brass, copper, steel or aluminum and is about 1 to 50 mm thick. The holes 42 are generally of from about 1 to 25 mm in diameter. The charging plate 40 is typically about 25 to 100 times as thick as the diameter of the orifices 28 and the diameter of the holes 42 is typically about 10 to 50 times the diameter of the orifices. The charging plate is positioned so that the jets from the orifices break into droplets as they pass through the holes in the plate. When the plate 40 is held at a voltage with respect to the liquid jet, the combination of this voltage and the capacitance between the plate and jet brings a charge to the section of the jet passing through the holes 42. As each droplet 44 breaks from the jet stream, it retains a portion of the charge. With charging, the droplets repel each other in flight and scatter into a cone shape as they fall towards the substrate 50. The amount of scatter can be controlled by varying the charging voltage.

The monitoring system 15 comprises a CCD video camera 46 with a microscopic zoom lens and a strobe-light 48 that is synchronized with the piezo driving signal. The monitoring system may also include a second strobe for measuring droplet velocities which can be of importance for certain applications such as spray forming and coating. The monitoring system takes real-time pictures of the droplet stream. These picture provide feedback that allows an operator to control droplet size and to adjust the pressure differential and vibration frequency to avoid satellite droplet formation.

The spray chamber 12 is an air-tight sealed chamber which maintains a substantially oxygen-free atmosphere which is beneficial for proper droplet formation. The spray chamber 12 is made from any suitable, preferably translucent, material including acrylic and glass.

The substrate 50 used in this embodiment to collect the metal droplets may be made from any suitable material including metal, ceramic, and glass. The substrate may also be connected with a heating/cooling system (not shown) and a height adjustment mechanism 52 for adjusting the height of the substrate in the spray chamber 12.

In operation, the process using the apparatus of FIGS. 1 and 2 is carried out by first inserting metal material in the form of chips, ingots, or shot into the container 16. Any suitable metals such as tin, zinc, lead, aluminum, titanium, iron, nickel, as well as mixtures or alloys thereof may be used depending upon the end use

application. The container and spray chamber are then sealed and flushed with an inert gas such as N_2, Ar or He to remove the oxygen. The container and metal material are then heated until the metal material melts and the temperature is then maintained at or above the melting temperature of the particular metal material. The function generator 25, amplifier 27, transformer 29 and oscilloscope 31 are then turned on to apply a signal of from about 100 to 300 volts at about 1 to 100 kHz. This signal vibrates the piezo transducer 22 which vibrates the shaft 24 and disk 25 and thus the melted metal. By applying a pressure differential between the container and spray chamber the liquefied metal is forced through the orifice or orifices 28 in the bottom of the container 16. A potential of about 50 to 5000 volts is applied to the charging plate 40 and as the liquefied metal jet passes out of the orifices 28 and through the hole or holes in the charging plate, it breaks-up into uniformly sized droplets which are charged. These metal droplets then continue their descent. The actual charge imparted on each droplet is a function of the diameter of the droplet, the diameter of the hole in the charging plate through which the droplet has passed, and the voltage between the charging plate and the liquid metal jets. A charge on a droplet on the order of 10^{-7} coulombs/gram is currently preferred. Depending on the end use, the metal droplets may solidify in flight or remain in a semiliquid or liquid state at the point they reach the substrate or collecting surface.

As defined herein uniformly sized metal droplets means that the droplets produced under defined process and equipment conditions, are substantially spherical in shape and vary in diameter by not more than about $\pm 25\%$, preferably by not more than about $\pm 10\%$, still more preferably by not more than about $\pm 5\%$, still more preferably by not more than about $\pm 3\%$, and most preferably by not more than about $\pm 1\%$. This process and apparatus is capable of producing metal droplets having sizes ranging from about 10 to 500 micro-meters in diameter.

An alternative embodiment of the present invention is shown in FIG. 3. In this embodiment like parts have the same reference numerals as in the embodiment of FIGS. 1 and 2. Such parts function in the same or similar manner. As shown, the charged metal droplet apparatus 60 comprises a container 66 having a temperature controller 30 and heating elements 33 for liquefying the metal 76 within the container 66. Unlike the embodiment of FIGS. 1 and 2, the charge is applied to the metal before it is formed into droplets by charging the liquefied metal 66 in the container using charging means 70. A suitable charging means would be a Van de Graaff generator.

Like the container of FIG. 2, container 66 has an orifice 68. Although only one spray orifice is shown, the container may have a plurality of spray orifices. The orifices are produced of the same materials as the orifices of the container of FIG. 2 and have diameters of about 2 and 10 mm. As the liquefied metal 76 is forced out of the container 66 through the orifice 68 it is subjected to oscillating gas jets 74 of an inert gas such as nitrogen, argon or helium. The gas jets 74 oscillate at a frequency of from about 1 to 500 kHz. A pulsed gas supply 72 is fed to the gas jets 74. The gas has a velocity between about 50 and 1,000 m/sec. The jet of liquid metal, once contacted by the oscillating gas jets which result in gas pulses, breaks up into a narrow distribution of metal droplets that is narrower than the distributions which are generated by conventional gas atomization

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techniques which do not use the oscillating gas jets. The spray chamber also contains a substrate 50 for the collection of the metal droplets.

Alternatively, either the metal droplet forming procedure using pulsed gas atomization may be used with a charging plate or the metal droplet forming procedure using vibratory means may be used with a charging of the liquefied metal in the container, i.e. before forming droplets of the metal.

The charged uniformly sized metal droplet apparatus and process of the present invention may be used in for a variety of different commercial and research applications. They are useful in the production of uniformly sized metal powders. With the apparatus and process of this invention, no seiving or other size classification procedures are required to obtain uniformly sized powders. The apparatus of the present invention is also useful in rapid solidification research on a droplet source that can be controlled to repeatedly produce droplets having specified diameters, initial velocities and thermal states. The apparatus can be used to produce single droplets by either selectively charging a single droplet and deflecting it or by charging all the droplets in a stream but one and then deflecting away the unwanted charged droplets.

The apparatus can also be used to perform fundamental experiments on spray forming that will explain how different droplet impact states determine process yield and the porosity and microstructure of sprayed deposits. In addition the apparatus can be used to seek distributions of droplets that can be produced by processes that are more efficient than gas atomization, but that produce deposits of the same or better quality as gas atomized sprays. By arranging the device's orifices in a line or long array, the apparatus can be used for the spray forming of metal sheets. It is difficult to spray form sheets with current spray forming techniques (that produce gaussian mass-flux distributions) because sheets must be nearly flat to be rolled. In conjunction with a device that sprays oppositely charged ceramic particles, the apparatus of the present invention can be used to spray form metal-matrix composites with excellent reinforcement distribution. The droplets and reinforcements attract each other in flight and produce a more homogeneous distribution than can be produced by random mixing.

The apparatus can be used to deposit uniform metal droplets onto a surface. Metal coating with this device may prove to be an effective method for applying metal coatings that have uniform properties and that are uniformly thick.

The apparatus and process of the present invention will now be described with reference to the following examples, which are illustrative of one of the embodiments of the present invention.

EXAMPLE I

Using an apparatus substantially as shown in FIGS. 1 and 2, chips of tin metal (500 g) were placed in a 304 stainless steel container. The tin was heated to a temperature of 300° C. to melt it. The tin was maintained at this temperature for the duration of the process. The spray chamber (a cast acrylic tube) and container were both flushed with N_2 gas and an atmosphere of substantially pure N_2 gas was maintained in both. A pressure differential of 40 psi was built up between the container and the spray chamber forcing the tin through a single orifice of a sapphire jewel (100μ in diameter) in the bottom

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of the container. At the same time, a function generator, amplifier, and transformer drove a lead metaniobate piezo-electric transducer with 300 volts at 15 kHz. At these conditions, the 3.2 mm thick crystal vibrated with an amplitude of 10^{-7} m. These vibrations were transmitted down the shaft through the disk and into the tin. The piezo crystal was positioned 20 cm away from the tin melt.

The jet of tin passed through the orifice in the bottom of the container and through a hole (3.2 mm in diameter) in a 6.4 mm thick charge plate positioned 2 mm below the bottom of the container. The charge plate was made of brass and was 5 cm in diameter. The charge plate was held at a potential of 400 volts with respect to the jet of tin. As the jet of tin passed through the hole in the charge plate it broke up into uniformly sized metal droplets which became charged and held a charge of 10^{-12} Coulombs. The droplets fell 1.5 m to a glass substrate whereon they were collected. The droplets were solid when they contacted the substrate.

The diameters of the metal droplets were measured and were found to be 190 ± 5 μm. The droplets had an initial velocity of 9 m/sec. The droplet diameters were measured using a microscope and micrometer table. It is believed that the actual droplet diameter distribution is actually smaller than that stated, but the method of determining the diameters is not capable of proving this. The initial velocity of the droplets was determined by measuring the spacing between the droplets with a CCD video camera with a microscopic zoom lens and multiplying by the frequency at which the droplets were formed. The droplet formation frequency was assumed to be the frequency at which the piezo was driven.

EXAMPLE II

The procedure of Example I was repeated except that the vibration frequency was changed to 20 kHz. This caused the resultant charged metal droplets to have a diameter of about 170 μm, ±5 μm.

EXAMPLE III

The procedure of Example I was repeated except that the orifice diameter was changed to 45 μm and the vibration frequency was changed to 25 kHz. This caused the resultant charged metal droplets to have a diameter of about 100 μm, ±3 μm.

EXAMPLE IV

The procedure of Example I was repeated except that the orifice diameter was changed to 45 μm and the vibration frequency was changed to 30 kHz. This caused the resultant charged metal droplets to have a diameter of about 94 μm, ±3 μm.

What is claimed is:

1. A process for producing and maintaining charged uniformly sized metal droplets comprising the steps of:
   (1) liquefying a quantity of metal disposed in a container having at least one orifice to permit the passage of metal;
   (2) vibrating the liquefied metal in said container; and
   (3) forcing the vibrating liquefied metal through the at least one orifice;
   said method further including a step of placing a positive or negative charge on the liquefied metal, either before or after it exits the at least one orifice, the vibration thereof thereby causing said liquefied metal to form uniformly sized liquid metal droplets,

which droplets exhibit a degree of variation of less than about ±25% from the average droplet diameter, and the charging thereof causing said droplets to maintain their uniform size.

2. The process of claim 1, wherein said vibrating step includes applying at least one oscillating gas jet to the liquified metal as it exits the at least one orifice.

3. The process of claim 1, wherein the liquefied metal is charged after it exits the at least one orifice in the container.

4. The process of claim 3, wherein the placing of a positive or negative charge on the liquefied metal comprises using a charging plate having at least one opening therein aligned with the at least one orifice so as to permit the vibrated liquefied metal exiting the orifice to pass through the charging plate and become charged.

5. The process of claim 4, wherein the liquefied metal is forced through a plurality of orifices forming a plurality of streams of uniformly sized metal droplets and passing the droplets through a plurality of openings in the charge plate thereby forming a plurality of streams of charged uniformly sized metal droplets.

6. The process of claim 3, wherein the uniformly sized droplets have a diameter which is within the range of from about 10 to 500 μm and wherein the droplets exhibit a degree of variation of about ±5% of the average droplet diameter.

7. The process of claim 3, wherein said vibrating step includes applying at least one oscillating gas jet to the liquified metal as it exits the at least one orifice.

8. The process of claim 7, wherein the placing of a positive or negative charge on the liquefied metal comprises using a charging plate having at least one opening therein aligned with the at least one orifice so as to permit the liquefied metal exiting the orifice to pass through the charging plate.

9. The process of claim 7, wherein the uniformly sized droplets have a diameter which is within the range

of from about 10 to 500 μm and wherein the droplets exhibit a degree of variation of about ±10% of the average droplet diameter.

10. The process of claim 1, wherein the liquefied metal is charged when it is in the container before it is formed into droplets.

11. The process of claim 10, wherein said vibrating step includes applying at least one oscillating gas jet to the liquified metal as it exits the at least one orifice.

12. The process of claim 10, wherein the uniformly sized droplets have a diameter which is within the range of from about 10 to 500 μm and wherein the droplets exhibit a degree of variation of about ±5% of the average droplet diameter.

13. The process of claim 1, wherein the process further comprises depositing the charged droplets onto a substrate.

14. The process of claim 1, wherein the uniformly sized droplets have a diameter which is within the range of from about 10 to 500 μm and wherein the droplets exhibit a degree of variation of about ±5% of the average droplet diameter.

15. The process of claim 1, wherein the uniformly sized charged metal droplets have an initial velocity of from about 1 to 25 m/sec.

16. The process of claim 1, wherein the uniformly sized metal droplets are charged to about 10^{-5} to 10^{-8} Coulombs per gram.

17. The process of claim 1, further comprising applying an electric field in a flow path of the metal droplets to change their trajectories.

18. The process of claim 1, further comprising monitoring the charged metal droplets after formation to determine the sizes and the velocities of said liquid metal droplets.

19. The process of claim 1, wherein the process is performed in an inert gas atmosphere.

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United States Patent [19]

Green et al.

[11] **Patent Number:** **4,819,831**

[45] **Date of Patent:** **Apr. 11, 1989**

[54] **DROPLET GENERATING APPARATUS**

[75] Inventors: Gary J. Green, Yardley, Pa.; Frederick L. Dryer, Pennington, N.J.; Dennis E. Walsh, Richboro, Pa.

[73] Assignee: Mobil Oil Corporation, New York, N.Y.

[21] Appl. No.: 99,860

[22] Filed: **Sep. 22, 1987**

Related U.S. Application Data

[60] Division of Ser. No. 917,288, Oct. 9, 1986, Pat. No. 4,717,049, which is a continuation of Ser. No. 596,990, Apr. 5, 1984, abandoned.

[51] Int. Cl.^{4} B65D 47/18
[52] U.S. Cl. 222/420; 261/76
[58] Field of Search 222/420, 422, 566, 630, 222/571, 255, 262, 263; 73/861, 861.41; 604/251, 253, 65; 422/99; 261/76, 116

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Primary Examiner—Joseph J. Rolla
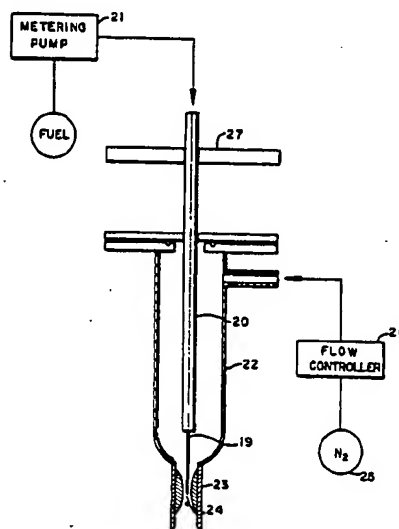*Assistant Examiner*—Kenneth Noland
Attorney, Agent, or Firm—Alexander J. McKillop; Charles J. Speciale

[57] **ABSTRACT**

Uniform droplets of a liquid are produced by positioning the end of a capillary tube in the throat of a venturi. Gas flowing through the venturi detaches droplets from the end of the capillary tube without requiring high volume gas flow or excessively high velocity of the droplets.
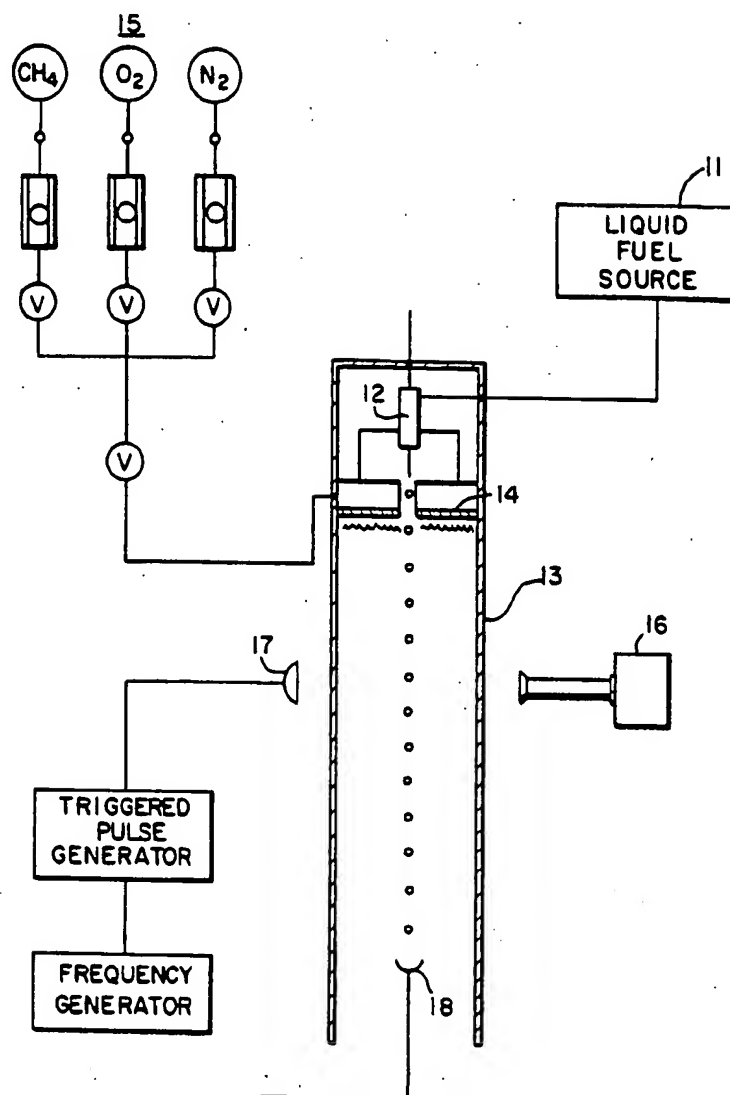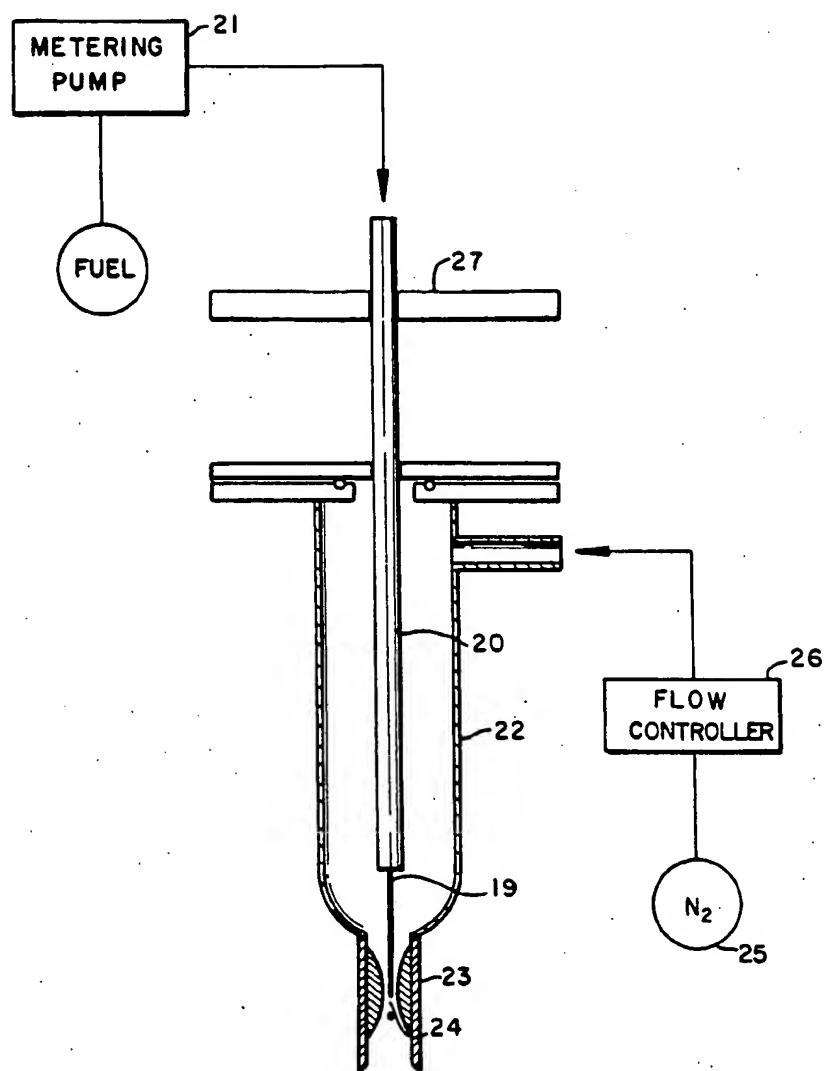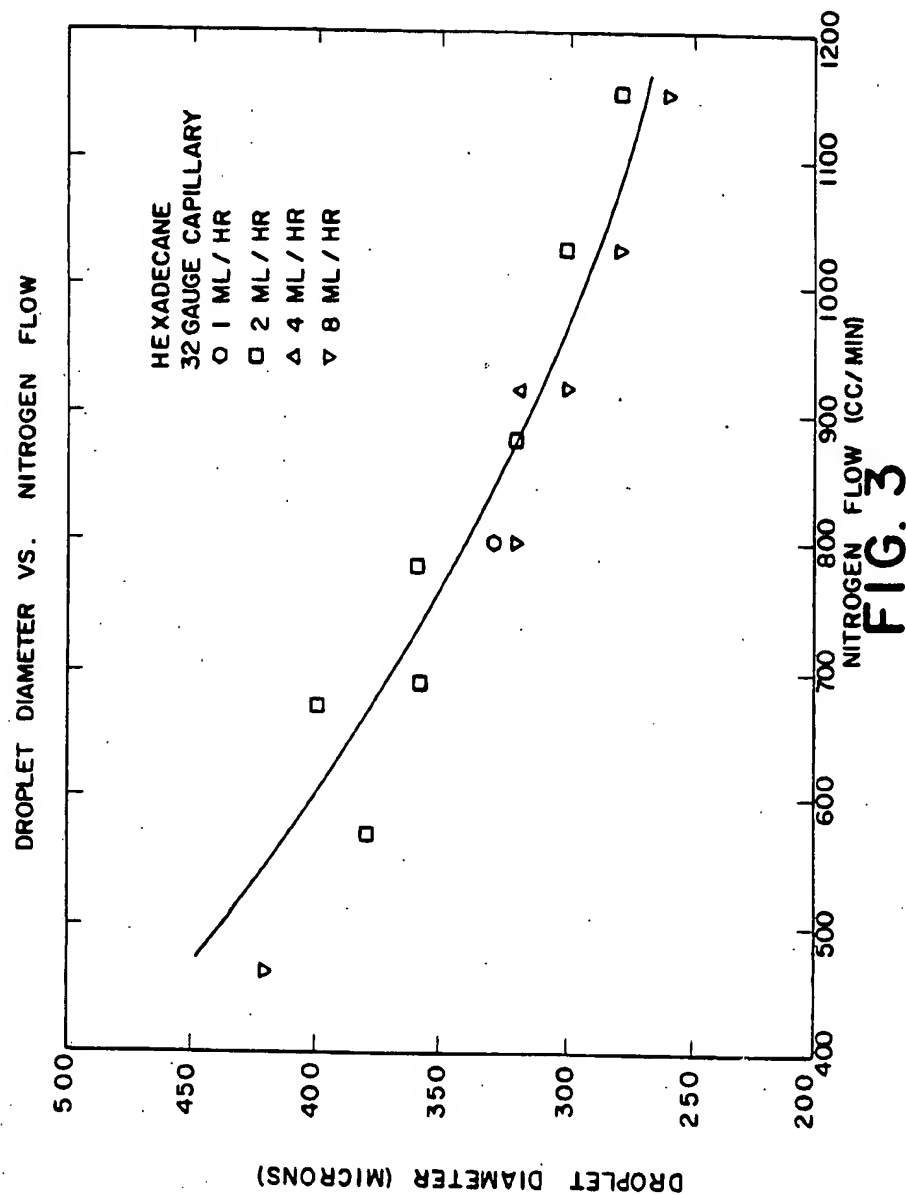
19 Claims, 7 Drawing Sheets

FIG. I

FIG. 2

DROPLET DIAMETER VS. NITROGEN FLOW

HEXADECANE
32 GAUGE CAPILLARY
O 1 ML / HR
□ 2 ML / HR
△ 4 ML / HR
▽ 8 ML / HR

NITROGEN FLOW (CC/ MIN)

DROPLET DIAMETER (MICRONS)

FIG. 3

DROPLET SPACING VS. NITROGEN FLOW

HEXADECANE
32 GAUGE CAPILLARY
O 1 ML/HR
□ 2 ML/HR
△ 4 ML/HR
▽ 8 ML/HR

NITROGEN FLOW (CC/MIN)

DROPLET SPACING (MM)

FIG.4

FIG. 5

FIG. 6

INITIAL DROPLET VELOCITY VS. NITROGEN FLOW

HEXADECANE

32 GAUGE CAPILLARY

FIG. 7

NITROGEN FLOW (CC/MIN)

AVG. INITIAL DROPLET VELOCITY (M/SEC.)

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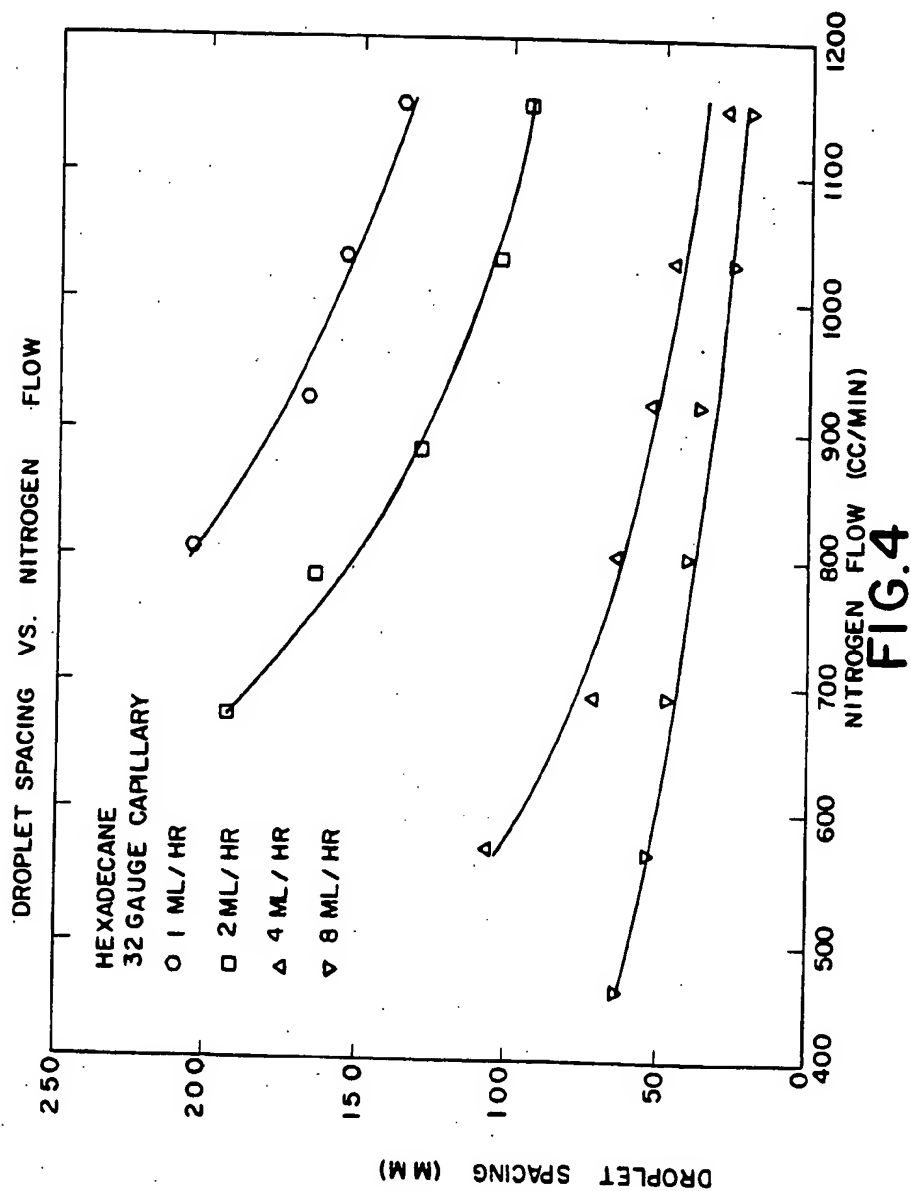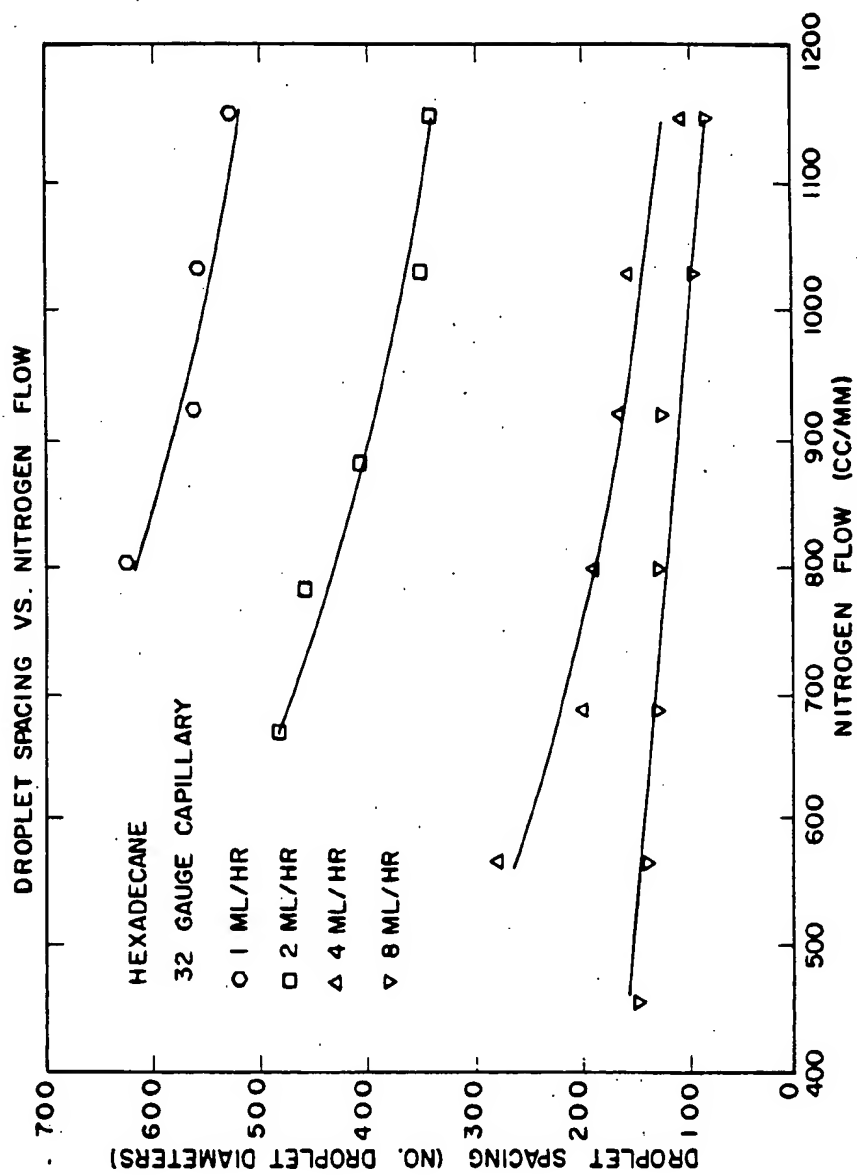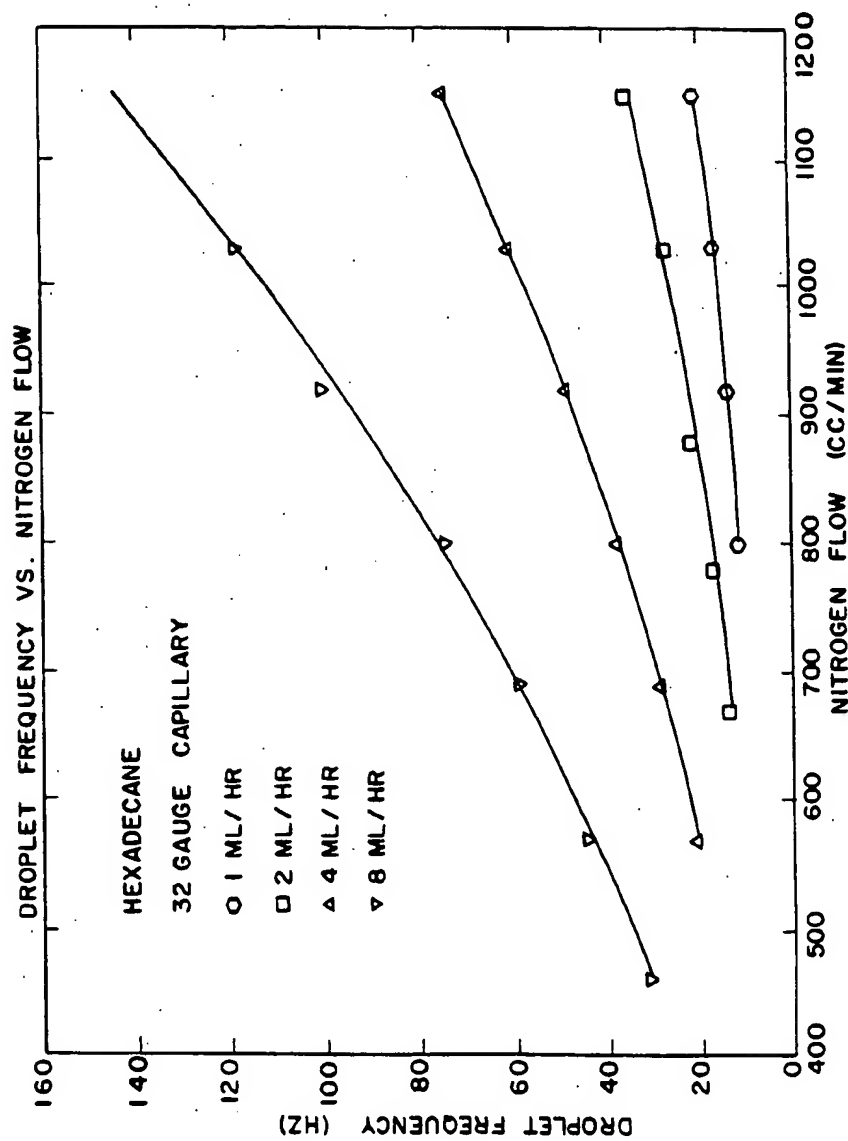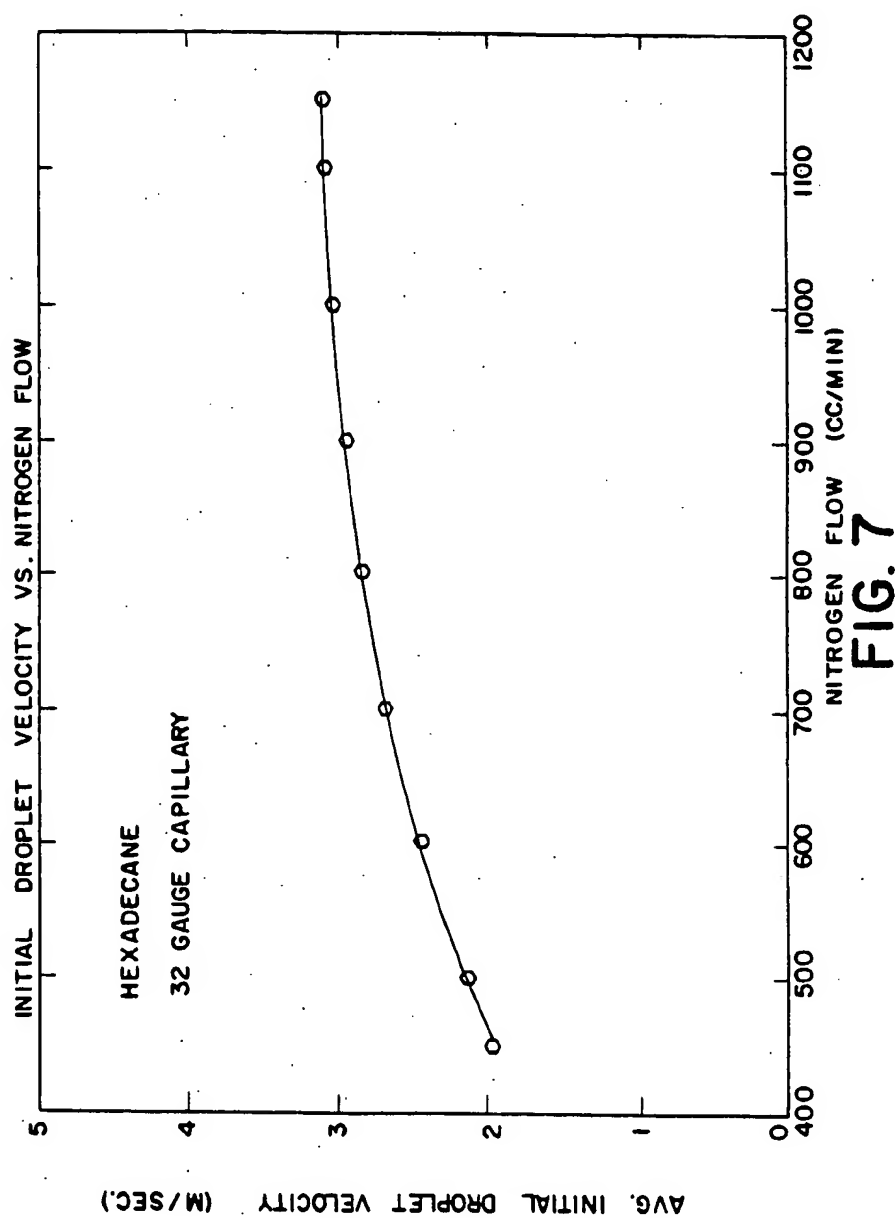
DROPLET GENERATING APPARATUS

This is a divisional of copending application Ser. No. 917,288, filed on Oct. 9, 1986 now U.S. Pat. No. 4,717,049, which is a file wrapper continuation of application Ser. No. 596,990, filed Apr. 5, 1984, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the generation of small, widely spaced droplets of uniform size and more particularly, to the generation of such droplets by placing the end of a capillary tube in a venturi throat.

A need exists in laboratory experimentation and in scientific analyses for the production of a stream of uniform, isolated droplets of liquid. Streams of small, uniformly-sized droplets are required, for example, in testing aerosol standards for environmental toxicological studies, ink jet printing methods, new nebulization techniques for flame atomic absorption spectroscopy, novel means for investigating fast chemical reaction kinetics, and new approaches to studying the combustion behavior of fuels. Several techniques are currently used for producing streams of small uniform droplets suitable for such applications. See, for example, J. J. Sangiovanni and A. S. Kestin, Combustion Science and Technology 16, 59 (1977); J. C. Lasheras, A. C. Fernandez-Pello, and F. L. Dryer, Combustion Science and Technology 21, 1 (1979); C. H. Wang, X. Q. Liu and C. K. Law, Paper No. 82-81, Fall Western States Meeting, The Combustion Institute, Sandia Laboratories, Livermore, CA Oct. 11–12, 1982.

The prior art includes Rayleigh instability and mechanical chopping techniques of producing droplets which rely on physically breaking up an established high velocity liquid jet by electromagnetically induced mechanical vibrations or high speed rotary shuttering, respectively. Piezoelectric techniques can be used to expel droplets by mechanical constrictions applied to a liquid reservoir. The use of moving parts or electronic components for the production of droplets gives rise to the possibility of component failure, or drift, which adversely affects repeatability with time.

A major restriction to the use of Rayleigh instability for exploring isolated droplet combustion is the limited droplet spacing inherently available. However, no alternative droplet generation techniques (e.g., mechanical chopping or piezoelectric techniques) producing well-spaced ($\geqq 30$ droplet diameters) droplets have been described which are adaptable for use in combustion apparatus without introducing significant experimental complexities. J. A. Bolt and M. A. Saad, "Combustion Rates of Freely Falling Fuel Droplets in a Hot Atmosphere", Sixth Symposium (International) on Combustion, p. 717, The Combustion Institute, 1957, describes an apparatus for forming fuel droplets by a small bore tube from which the drops are thrown by a concentric jet of air. Droplet size is controlled by capillary bore size, pressure of the concentric air head, head of the fuel and the distance the capillary protrudes beyond the air nozzle. Resultant droplets are ~1.1 mm in diameter, much larger than those found in typical combustion systems. In the laboratory, as well as practical combustion devices, there exists a limited droplet residence time within the combustor during which complete burnout must be achieved. Very large droplets (such as those described above) would require inordinately large

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combustion chambers to approach complete or nearly complete burnout. Note that the device of Bolt and Saad resulted in droplets which burned to ~300 μ diameter over the length of their combustor, far from complete burnout.

It is an object of the invention to provide apparatus for producing uniform droplets of controlled, substantially smaller size in which the droplet spacing, and initial velocity can be regulated.

SUMMARY OF THE INVENTION

In accordance with the present invention droplets are induced by a venturi throat which produces high velocity gas flow to detach uniform droplets from the end of a capillary tube. In accordance with the invention, the venturi includes a converging-diverging nozzle which forms droplets with good trajectory, and with the desired droplet size and spacing. The present invention alleviates problems associated with prior art apparatus including problems of droplet size and spacing, restricted operating ranges, significant liquid volume requirements, and cost and complexity of the apparatus found in the prior art.

The foregoing and other objects, features and advantages of the invention will be better understood from the following more detailed description and appended claims.

DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the droplet producing apparatus of the present invention in a system for measuring the combustion of fuel;

FIG. 2 shows the droplet generation device of the present invention;

FIG. 3 shows droplet diameter versus nitrogen flow in an exemplary practice of the invention;

FIG. 4 shows droplet spacing versus nitrogen flow in an exemplary practice of the invention;

FIG. 5 shows droplet spacing versus nitrogen flow in an exemplary practice of the invention;

FIG. 6 shows droplet frequency versus nitrogen flow; and

FIG. 7 shows initial droplet velocity versus nitrogen flow in an exemplary practice of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

FIG. 1 depicts a source of liquid fuel 11 to be tested. The liquid fuel is supplied to the droplet generation device 12 of the present invention.

Droplets are produced in the combustion duct 13 which has a flat flame burner 14 supplied with fuel, oxygen and nitrogen from the sources shown at 15.

Optical detection of the combustion process is performed by a detector 16 such as a camera or optical probe, and a triggered light source 17. The residue of the combustion process is collected in sample collection probe 18.

Referring to FIG. 2, the droplet generation device of the present invention includes a capillary tube 19 having a liquid receiving end which is connected to the tube 20 which contains fuel from the metering pump 21. An outer concentric tube 22 has a venturi 23 at the bottom thereof. The tip of capillary tube 19 is positioned in the throat 24 of the venturi 23.

Venturi 23 is a converging-diverging nozzle with the diverging nozzle section having a half angle of 7.5° degrees in an exemplary embodiment. The converging-

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diverging nozzle insures a better trajectory of the droplets than other veturis.

Nitrogen gas from source 25 is supplied through flow controller 26 which regulates the flow of gas through the venturi to control the formation of droplets from the tip of the capillary tube. By varying the liquid flow, gas flow, and capillary size, the droplet size, spacing, frequency and initial velocity may be precisely controlled.

A stream of droplets is produced by inducing premature detachment of incompletely formed droplets at the tip of the capillary 19. This detachment is accomplished by drag caused by the annular flow of gas past the capillary tip which is positioned in the throat 23 of the venturi. The gas is accelerated past the tip of the capillary by the venturi and then decelerated upon exit from the throat of venturi 23. Droplets thus formed are much smaller in diameter than those that would result from natural detachment due to the weight of the droplet overcoming the interfacial tension at the capillary tip.

Precise metering of the liquid flow is controlled by the metering pump 21 and flow controller 26 accurately controls gas flow.

Accurate positioning of the capillary tip with respect to the venturi is accomplished with a micrometer driven translation stage 27. In an exemplary embodiment of the invention, a 32-gauge (0.004" inside diameter) stainless steel capillary was positioned in the throat of a venturi of approximately 1 mm inside diameter.

The critical relationship between the size of the venturi throat and the diameter of the capillary tube will depend on the type of droplets to be produced. For the testing of fuels as described herein, the capillary tube 19 has an inside diameter in the range of about 0.001" to 0.035" and outside diameter of 0.005" to 0.05". The outer concentric tube 22 has an inside diameter in the the range of 0.1" to 2", and the throat of the venturi 23 has an inside diameter in the range of 0.01" to 0.075", and a throat length in the range of 0.03" to 0.3".

Droplet characterization was carried out by a helium-neon laser aligned to intersect the path of the droplet stream. Scattered laser light from the droplets passing through the beam was detected with a photodiode miniprobe. Resultant modulated photodiode output signal was monitored with an oscilloscope to yield directly the droplet frequency, i.e., the rate of droplet production. The output signal was also supplied to a strobe lamp used to synchronously back illuminate the droplet stream for visual observation and photography to accurately measure droplet size and spacing.

The appearance of a hexadecane droplet emerging from the tip of the device was spherical and relatively well centered with respect to the tip. The extent of droplet spacing available with the present invention was shown by droplets spaced by 100 droplet diameters, a spacing 20–50 times greater than that obtained via Rayleigh instability techniques. The relationships between droplet size, spacing, and frequency associated with the current technique are distinctly different from those observed with the Rayleigh instability technique.

By observing droplet diameter and spacing for a variety of liquid and gas flow rates, the results depicted in FIGS. 3, 4, and 5 were obtained. FIG. 3 shows that droplet diameter decreases with increasing nitrogen flow past the capillary tip, relatively independently of the liquid flow rate through the capillary. FIG. 4 shows that inter-drop spacing also decreases with increased nitrogen flow. The magnitude of the spacing, however, clearly depends on the rate of liquid flow

through the capillary, viz. for a given nitrogen flow, the droplet spacing decreases with increasing liquid flow. FIG. 5 presents the droplet spacing data shown in FIG. 4 in terms of numbers of droplet diameters separating individual droplets. It is evident that droplet spacings from 100 to 600 droplet diameters may be achieved by simply varying the flow conditions across the ranges indicated in the figure.

The frequency of production of the resultant droplets as a function of operating parameters is illustrated in FIG. 6. Droplet frequency increases with increasing nitrogen flow and also increases with increasing liquid flow. The relatively low frequencies of 10–150 Hz produced in the invention should be contrasted to the 500–2000 Hz production rates observed in previous work on the Rayleigh instability technique. The low droplet production rates coupled with the relatively low liquid flow rates ($<$ 10 ml/hr) in the current device offer the advantage of greatly reduced liquid requirements compared to the Rayleigh instability technique which required 200–400 ml/hr liquid flow.

The initial velocity of droplets produced was also determined as a function of liquid and nitrogen flow by multiplying the initial droplet spacing by the droplet frequency. The collective results are plotted as a single curve in FIG. 7 and show that the initial droplet velocity has a mild dependence on nitrogen flow, gradually increasing with increasing flow. There is no clear dependence on liquid flow rate from the present data. Average initial droplet velocities are 2–3 m/s, comparable to those obtained with the Rayleigh instability technique and suitable for low Reynolds number studies of isolated droplet combustion in the current droplet combustion device. Studies with light No. 6 marine fueld have shown nominally the same behavior in terms of droplet size, spacing, frequency and velocity.

While a particular embodiment of the invention has been shown and described, various modifications are within the true spirit and scope of the invention. The claims are, therefore, intended to cover all such modifications.

What is claimed is:

1. A method of producing uniform droplets of a liquid comprising:

supplying a stream of gas to a concentric tube, said stream of gas flowing through said concentric tube;

supplying said liquid to a first end of a capillary tube positioned in said concentric tube;

accelerating said stream of gas toward said first end of said capillary tube; and

decelerating said stream of gas after said steam of gas passes said first end of said capillary tube;

wherein said accelerating stream of gas detaches uniform droplets of diameter less than 450 micrometers of said liquid from said first end of said capillary tube as said accelerating stream of gas flows past said first end of said capillary tube, said detached droplets being spaced apart by a distance in the range of 100–600 droplet diameters.

2. The method recited in claim 1 further comprising the steps of;

supplying said accelerating gas to a venturi throat; and

regulating the flow of gas through said venturi throat to control the formation of droplets from said first end of said capillary tube;

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wherein said uniform droplets of said liquid are de-
tached by said accelerating gas flowing through
said venturi throat.

3. The method recited in claim 1 further comprising
the step of:
controlling the flow of liquid to said capillary tube to
control the rate of droplet production.

4. The method recited in claim 3 wherein said liquid
is supplied at a flow rate less than 10 ml/hr.

5. A method of producing uniform droplets of a liquid
comprising:
supplying a stream of gas to a concentric tube;
supplying said liquid to an end of a capillary tube
positioned in said concentric tube;
accelerating said stream of gas toward said first end
of said capillary tube;
detaching uniform droplets of diameter less than 450
micrometers of said liquid from said first end of
said capillary tube by said accelerating stream of
gas as said accelerating stream of gas flows past
said first end of said capillary tube; and
decelerating said stream of gas upon detaching said
uniform droplets of said liquid from said first end of
said capillary tube, said detached droplets being
spaced apart by a distance greater than approxi-
mately 25 mm apart.

6. The method recited in claim 5 further comprising
the step of regulating the flow of said stream of gas to
control the formation of droplets from the tip of said
capillary tube.

7. The method recited in claim 5 further comprising
the step of controlling the flow of liquid to said capil-
lary tube.

8. The method of claim 5 further comprising the step
of determining the rate of droplet production.

9. The method of claim 5 further comprising the step
of measuring said droplet size.

10. The method recited in claim 5 further comprising
the step of:
supplying said accelerating gas to a venturi throat;
wherein said uniform droplets of said liquid are de-
tached by said accelerating gas flowing through
said venturi throat.

11. The method recited in claim 10 further compris-
ing the step of regulating the flow of gas through said
venturi throat to control the formation of droplets from
said first end of said capillary tube.

12. A method of producing uniform droplets of a
liquid comprising:
supplying a stream of gas to a concentric tube;
supplying said liquid to a first end of a capillary tube
positioned in said concentric tube to provide in-
completely formed droplets at said first end of said
capillary tube;
accelerating said stream of gas toward said first end
of said capillary tube;
supplying said accelerating gas to a venturi throat;

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detaching said incompletely formed droplets of said
liquid from said first end of said capillary tube to
produce uniform droplets spaced a distance greater
than approximately 25 mm apart, said detached
droplets being of diameter less than 450 microme-
ters and
decelerating said stream of gas after said stream of gas
passes said first end of said capillary tube.

13. The method recited in claim 12 further compris-
ing the step of regulating the flow of gas through said
venturi throat to control the formation of droplets from
said first end of said capillary tube.

14. The method recited in claim 12 further compris-
ing the step of controlling the flow of liquid to said
capillary tube to control the rate of droplet production.

15. The method recited in claim 14 wherein said liq-
uid is supplied at a flow rate less than 10 ml/hr.

16. A method of producing uniform droplets of a
liquid comprising:
supplying a stream of gas to a concentric tube, said
stream of gas flowing through said concentric tube;
supplying said liquid to a first end of a capillary tube
positioned in said concentric tube;
accelerating said stream of gas toward said first end
of said capillary tube;
decelerating said stream of gas after said stream of gas
passes said end of said capillary tube; and
controlling the flow of said liquid to said capillary
tube to control the rate of droplet production;
wherein said accelerating stream of gas detaches
uniform droplets of said liquid from said first end of
said capillary tube as said accelerating stream of
gases flows past said first end of said capillary tube,
said droplets being produced at a frequency be-
tween 10–150 hz.

17. The method recited in claim 16 wherein said liq-
uid is supplied at a flow rate less than 10 mil/hr.

18. A method of producing uniform droplets from a
liquid comprising:
supplying a stream of gas to a concentric tube;
supplying said liquid to a first end of a capillary tube
positioned in said concentric tube to provide in-
completely formed droplets at said first end of said
capillary tube;
accelerating said stream of gas toward said first end
of said capillary tube;
supplying said accelerating gas to a venturi throat;
detaching said incompletely formed droplets of said
liquid from said first end of said capillary tube;
decelerating said stream of gas after said stream of gas
passes said first end of said capillary tube; and
controlling the flow of said liquid to said capillary
tube to control the rate of droplet production;
wherein said droplets are produced at a frequency
between 10–150 hz.

19. The method recited in claim 18 wherein said liq-
uid is supplied at a flow rate less than 10 ml/hr.

* * * * *

(12) **United States Patent**

Jolliffe

(10) **Patent No.:** **US 6,586,731 B1**

(45) **Date of Patent:** **Jul. 1, 2003**

(54) **HIGH INTENSITY ION SOURCE APPARATUS FOR MASS SPECTROMETRY**

(75) Inventor: **Charles Jolliffe**, Schomberg (CA)

(73) Assignee: **MDS Inc.**, Concord (CA)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/548,281**

(22) Filed: **Apr. 12, 2000**

Related U.S. Application Data

(60) Provisional application No. 60/128,807, filed on Apr. 12, 1999.

(51) Int. Cl.[7] G01N 27/26; G01N 27/447

(52) U.S. Cl. .... 250/288; 250/281; 250/282; 250/299 R

(58) Field of Search 250/288, 282, 250/281

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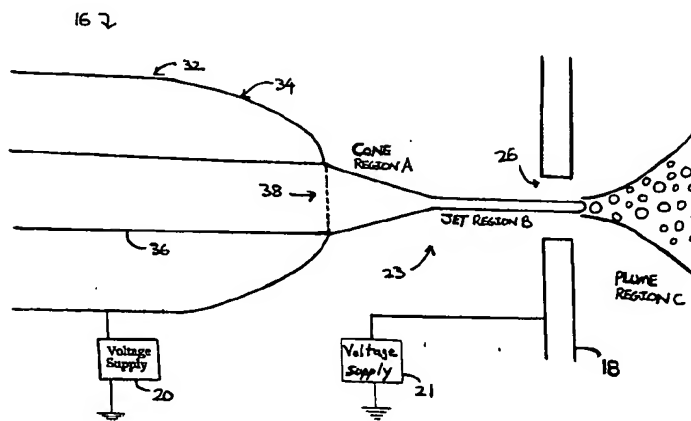
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Primary Examiner—John R. Lee
Assistant Examiner—David A. Vanore
(74) *Attorney, Agent, or Firm*—Bereskin & Parr

(57) **ABSTRACT**

A high intensity ion source for a mass spectrometer is provided having system dimensions and parameters which cause the Taylor cone of a liquid charge stream to pass through an aperture in a lens into a low pressure chamber without substantially desolvating. A capillary tube having an outlet diameter on the order of 50 micrometers is located in an ion source chamber which is maintained at close to atmospheric pressure. The outlet of the capillary tube is positioned at a distance on the order of 250 micrometers from the aperture of the lens. The low pressure chamber is maintained at a pressure on the order of 13 pascals. With a suitable applied field, a Taylor cone ion stream is formed and passes through the aperature in the lens into a low pressure chamber without substantially desolvating. Substantial desolvation of the liquid charge stream is accomplished through the application of heating techniques within the low pressure chamber.
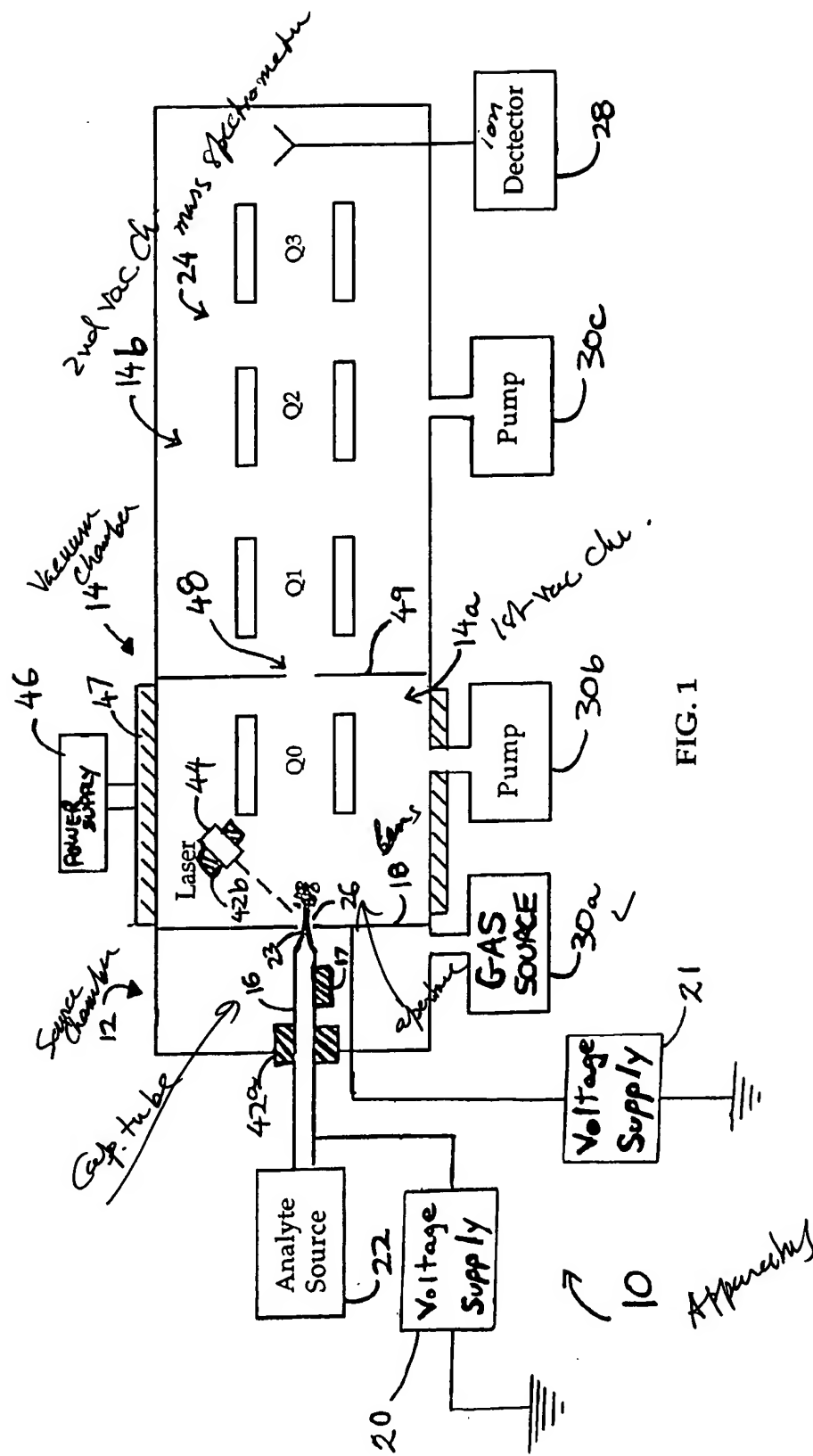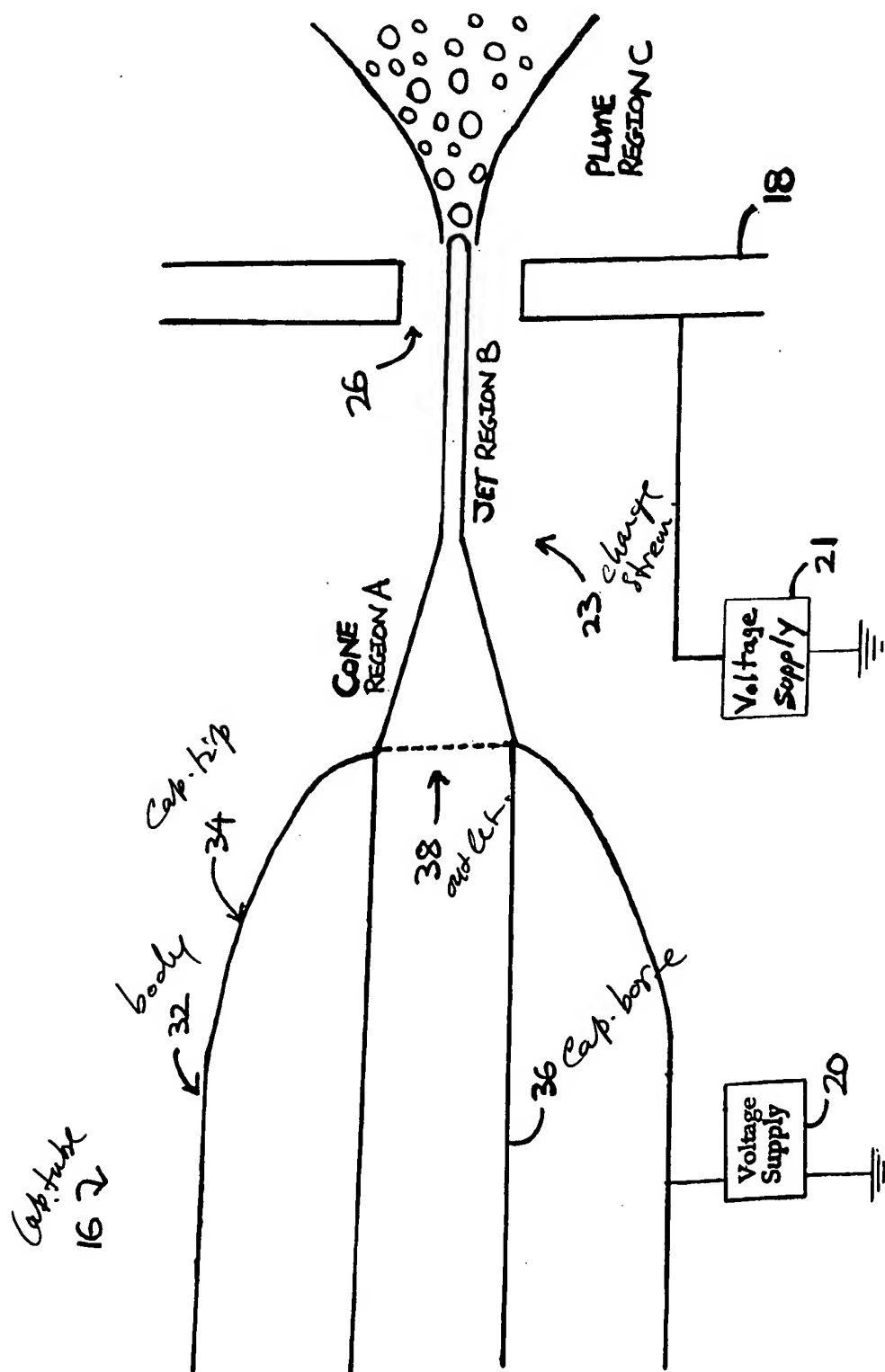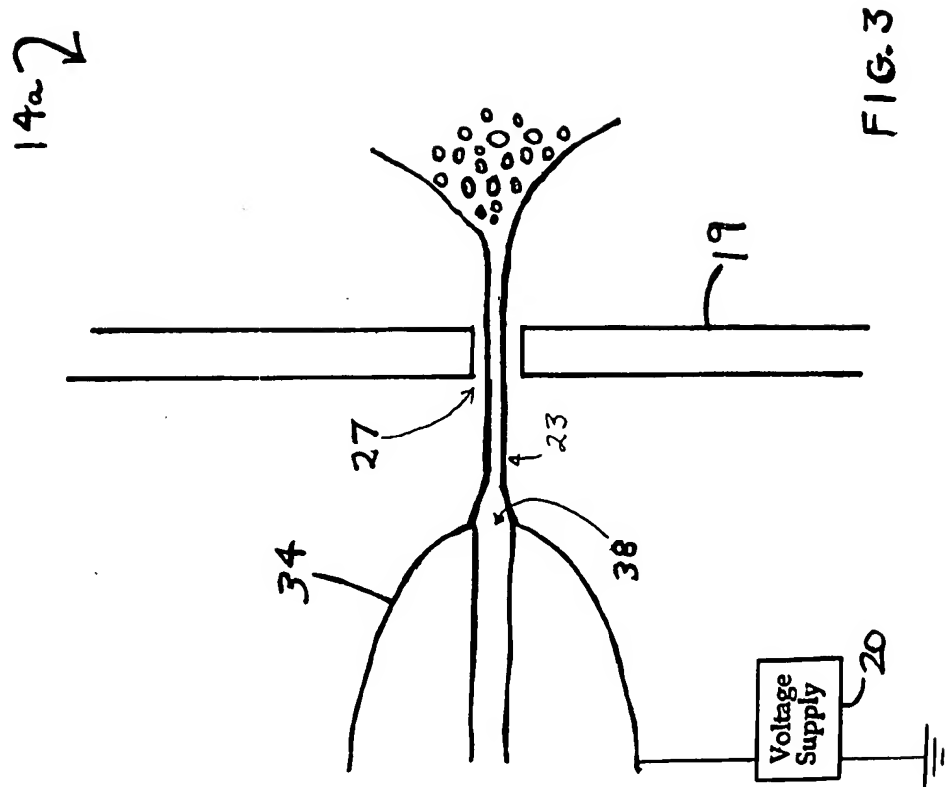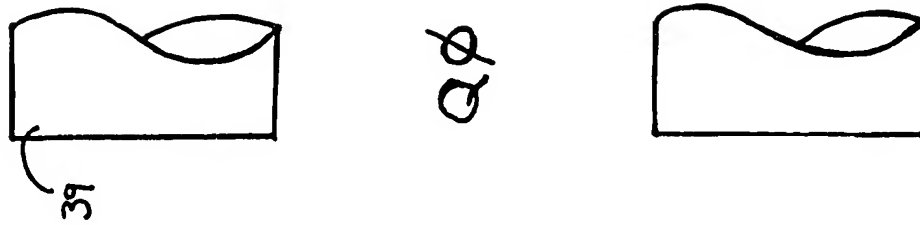
51 Claims, 8 Drawing Sheets

FIG. 1

FIG. 2

39

4φ

14a

19

27

23

34

38

Voltage Supply

20

FIG. 3

FIG.4

FIG.5a

FIG.5b

FIG.6

FIG. 7
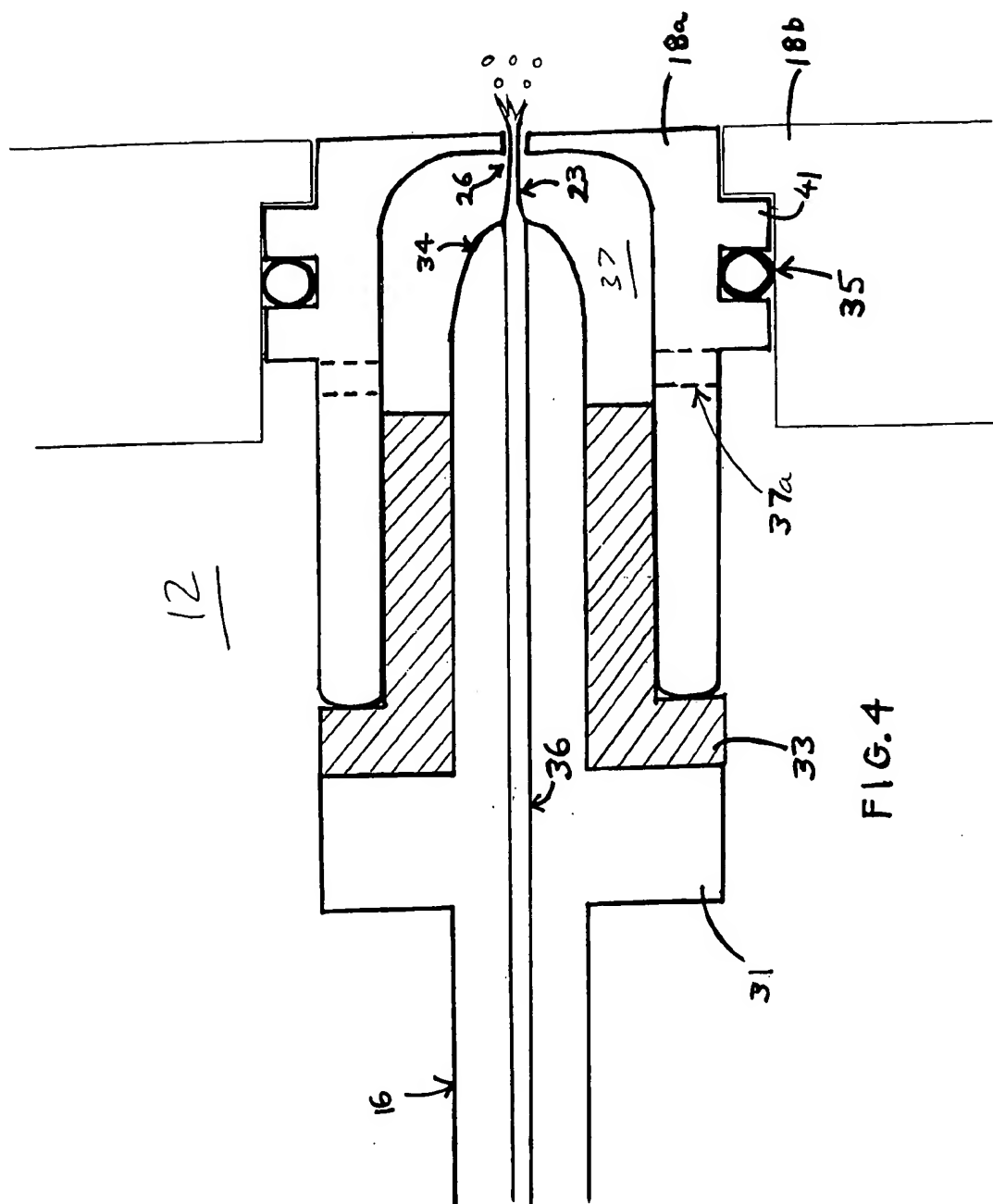
HIGH INTENSITY ION SOURCE APPARATUS FOR MASS SPECTROMETRY

This application claims the benefit of provisional application No. 60/128,807 filed Apr. 12, 1999.

FIELD OF THE INVENTION

The present invention relates to method and apparatus for forming ions from a liquid for use by an analytical instrument, typically a mass spectrometer.

BACKGROUND OF THE INVENTION

Various types of ion sources have been used in the past to produce ions from a liquid for mass spectrometers. Over the last decade the practise has been to produce the ions at or nea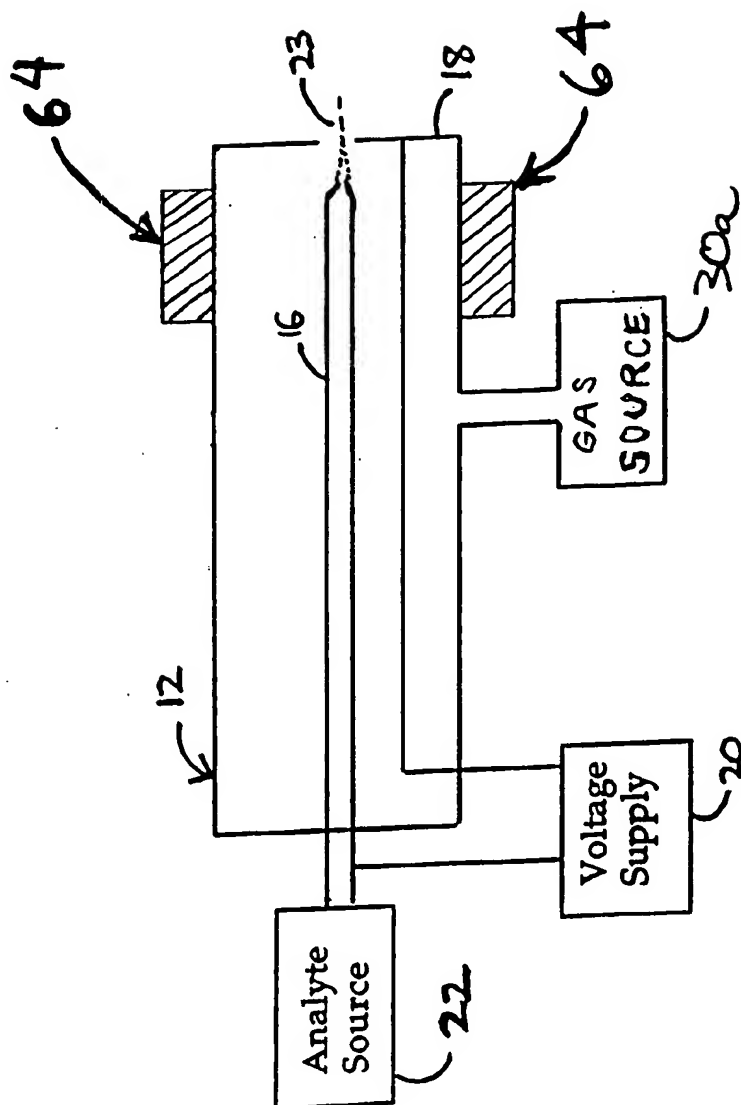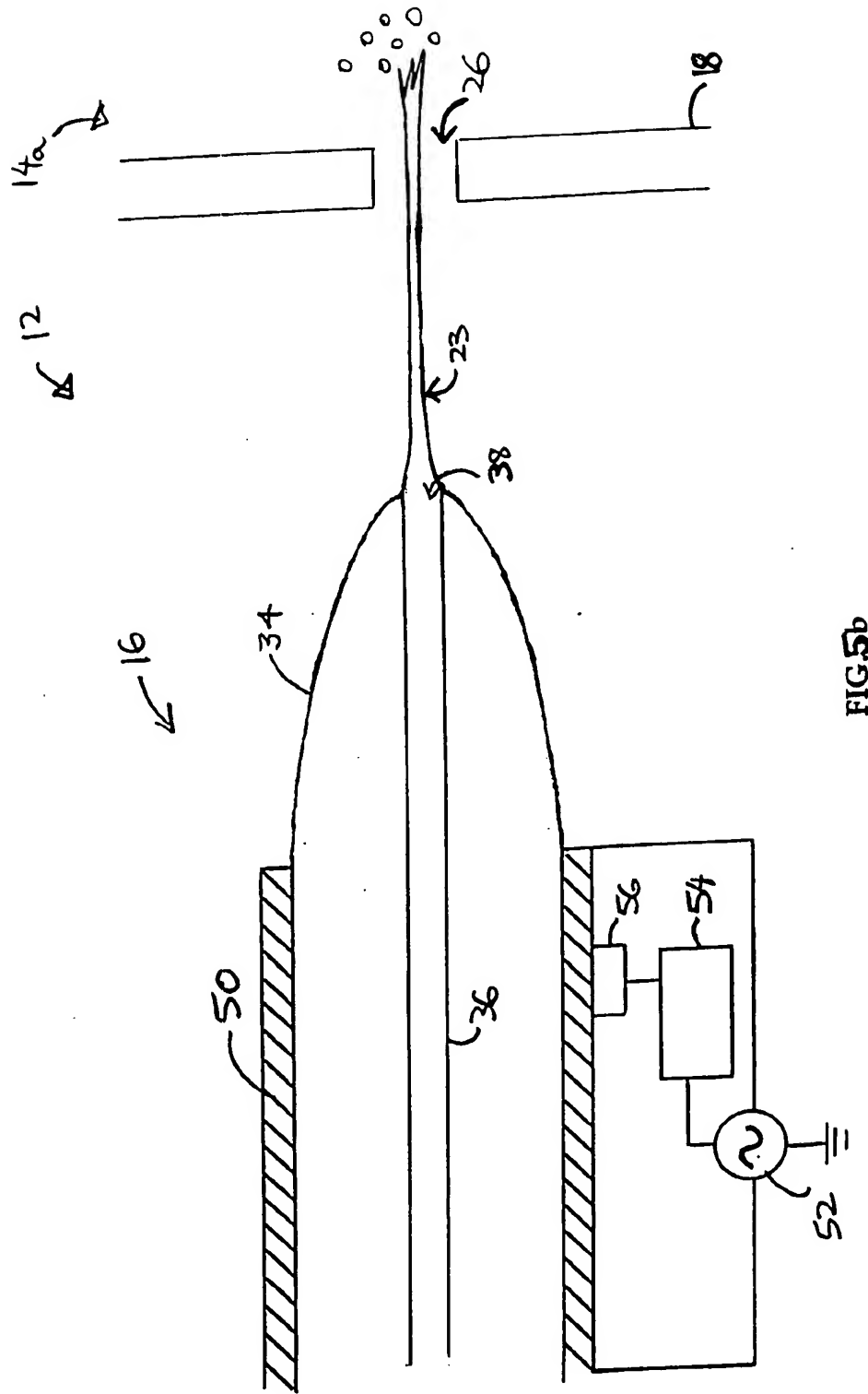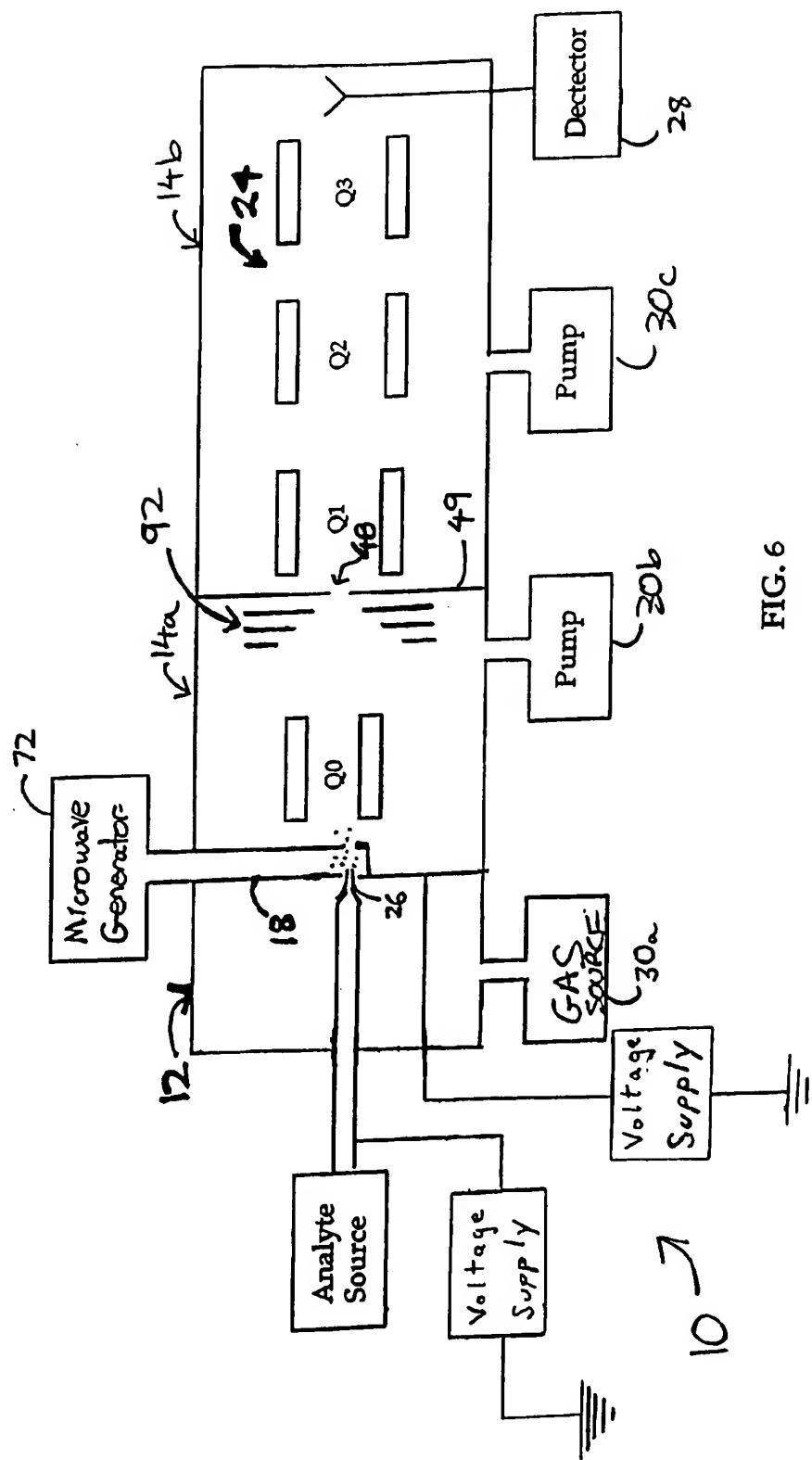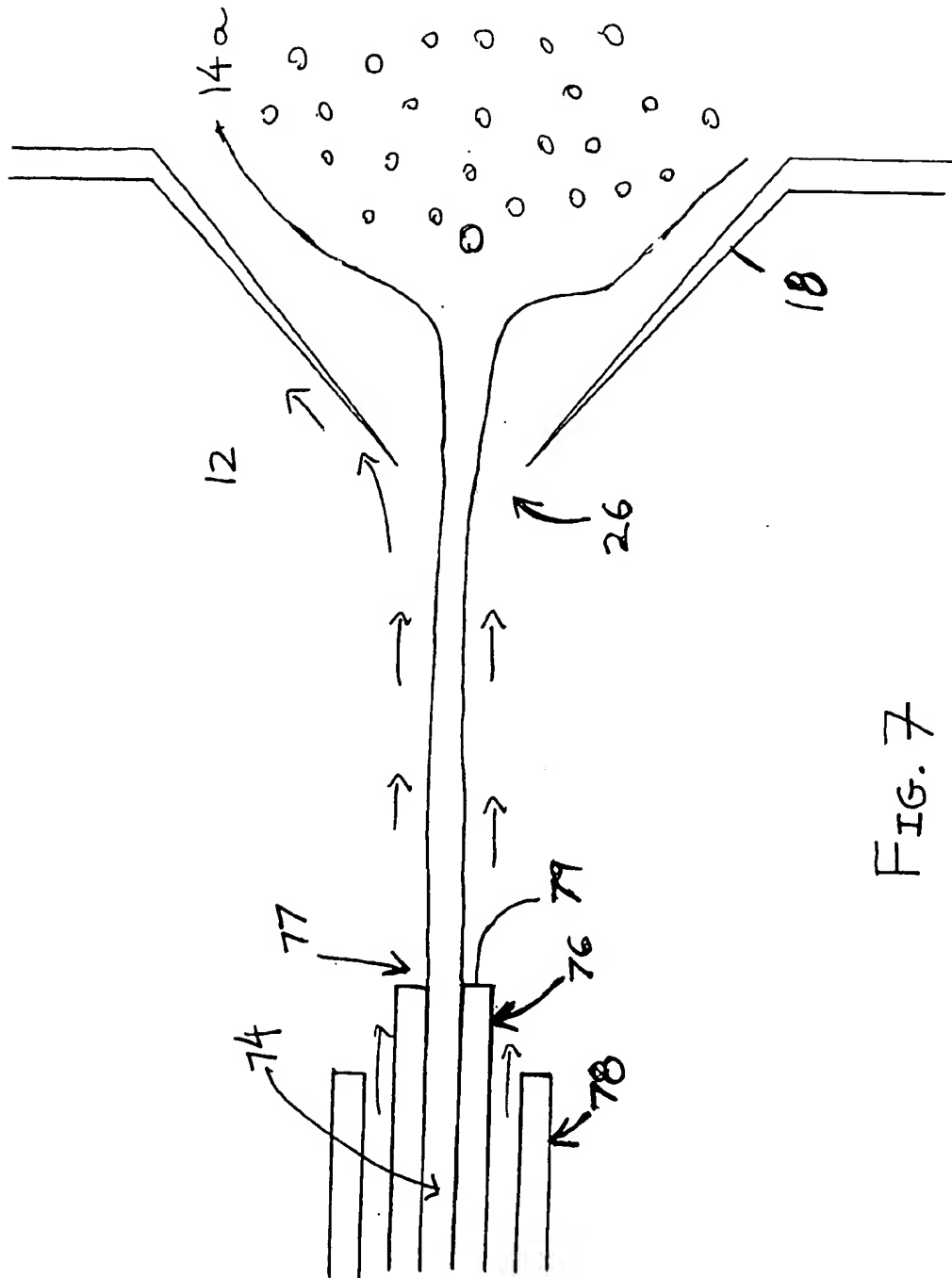r atmospheric pressure and then to direct the ions into a vacuum chamber which houses the mass spectrometer. Examples of these ion sources include the well known electrospray ion (ESI) source, discussed in U.S. Pat. No. 4,842,701 to Smith et al. and the ion source referred to as ion spray, described in U.S. Pat. No. 4,935,624 to Henion et al.

In its most basic form, an ESI source is created by applying a potential difference on the order of 5000 volts between a metal capillary and an interface lens in which there is an aperture. The distance between the capillary tip and lens is in the range of 1 to 3 centimeters. The analyte is contained in a solvent which is pumped through the capillary. As the liquid emerges from the capillary tip, the high electric field causes charge separation and a subsequent rapid increase of the charged liquid flow velocity accompanied by a sharp reduction of liquid flow diameter, and assuming a shape called a Taylor cone. Within a short distance of the capillary tip, the mutual charge repulsion within the liquid exceeds the ability of the surface tension to contain the liquid, resulting in a scattering of the smooth liquid flow into liquid droplet form. The maximum flow rate of the ESI source is about 5 microliters/minute (μL/m). Much higher flow rates cause the ion signal to decrease and become unstable because of the advent of larger droplets which take too long to desolvate. Consequently much of the ion current becomes bound up in droplets instead of gas phase ions. ESI sources are typically operated at or near atmospheric pressure, because a high heat transfer rate to the droplets required for evaporation is possible due to the high rate of droplet-air molecule collisions.

Prior art ion spray devices can include a concurrent flow of high velocity gas coaxial with a capillary tube. This gas nebulizes the liquid flowing from the capillary tip, effectively resulting in smaller sized droplets. Adding an external source of heated gas results in the effective evaporation of liquid flow up to 1000 microliters per minute.

In some configurations of ion spray or electrospray sources, the metal capillary has been replaced by a nonconductive capillary such as fused silica. The electrical connection to the liquid is usually made at a metal junction upstream from the capillary tip and relatively close to the tip (e.g. 10 cm).

Although ion spray has replaced electrospray in the flow range from about 1 microliter/minute to 1000 microliter/minute, ESI sources called "nanospray" which use extremely low flows of the 1 to 20 nanoliters per minute range are becoming popular for situations where the amount of sample is limited. The nanospray source is distinguished from the higher flow rate sources by having a smaller capillary diameter, and both a lower distance and potential difference between the capillary tip and the lens. The small

nanospray capillary bore produces small droplets which quickly evaporate. For example, a typical nanospray source is placed at a distance of between 1 and 3 millimeters from the lens and a typical electrospray source is placed at a distance of between 1 to 2 centimeters from the lens. In addition, due to the very low flow rate of the nanospray source, a large fraction of the ion current from the capillary passes through the aperture of the lens, whereas for the high flow sources, this same fraction is often less than one percent. In both cases, the ion current through this lens aperture is predominantly in the form of desolvated gas phase ions, that is, not in liquid form.

Regardless of the source design, the sensitivity of all atmospheric source designs generally increases with a larger aperture in the lens. Larger apertures are increasingly used to collect more ion current emerging from the capillary, but with a typical fixed ion/gas ratio of ions and gas through the lens aperture, more gas is present which necessitates higher capacity and costly vacuum pumps to maintain the mass spectrometer vacuum pressure. A typical ion/gas ratio for the atmospheric sources is from one ion in 10^9 to 10^{10} molecules of air, usually nitrogen.

Attempts have been made to increase the number of ions that can be delivered to a low pressure region by providing electrospray directly into a low pressure region as disclosed in U.S. Pat. No. 5,838,002 to Sheehan, where a potential difference is applied across an electrospray capillary positioned in an evacuated chamber of less than 13 pascals and a counter electrode. This approach is limited by corona discharge which can produce chemical noise, and liquid boiling which disturbs the Taylor cone and causes severe signal instability and signal reduction.

Accordingly, there is a need for a method and apparatus for providing an improved flow of ions into vacuum from an electrospray source such that a low volume of gas is admitted into the vacuum chamber along with the ions, such that corona effects are avoided, such that boiling does not occur, and such that the lab footprint of requisite pumping equipment is reduced.

BRIEF SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an apparatus for providing gas phase ions in a relatively low pressure region from a liquid, the apparatus comprising:

(a) a capillary tube, said capillary tube having an input for receiving the liquid, a longitudinal bore, and an outlet for discharging said liquid at a preset flow rate into a first region at a relatively high pressure;

(b) a first interface element with an aperture therein and separating said first region from a second region at a relatively low pressure;

(c) an electrode located downstream from the aperture of the capillary tube; and

(d) a voltage source for generating a voltage potential between said liquid in the capillary tube and said electrode;

wherein the aperture of the capillary tube is aligned with the aperture of the first interface element and is positioned directly in front of, and in close proximity to, the aperture of the first interface element, whereby, in use, with a sufficient voltage potential applied between the liquid and the electrode to form an electric field sufficient to cause the liquid stream flowing through the outlet of the capillary tube at the preset flow rate to become a charged liquid stream that originates at the aperture of the capillary tube and flows through the aperture of the first interface element into the

second region and substantially desolvates into gas phase ions in the second region, and wherein the spacing between the aperture of the capillary tube and the aperture of the first interface element is such that there is minimal expansion of the liquid charge stream in the first region.

In a second aspect, the present invention provides an apparatus for providing gas phase ions in a relatively low pressure region from a liquid including a matrix material, the apparatus comprising:

(a) a capillary tube, said capillary tube having an input for receiving the liquid, a longitudinal bore, and an outlet for discharging said liquid at a preset flow rate into a first region at a relatively high pressure;

(b) pulsing means coupled to the capillary tube for providing a series of pressure pulses to the liquid within the capillary tube to cause said capillary tube to expel a series of liquid charge stream droplets;

(c) a first interface element with an aperture therein and separating said first region from a second region at a relatively low pressure;

(d) desolvation means for desolvating the liquid charge stream droplets into gas phase ions in the second region;

wherein the aperture of the capillary tube is aligned with the aperture of the first interface element and is positioned directly in front of, and in close proximity to, the aperture of the first interface element, whereby, in use, when said pulsing means provides sufficient pulsing action to the capillary tube to cause the liquid stream flowing through the aperture of the capillary tube at the preset flow rate to become a pulsed liquid stream that originates at the aperture of the capillary tube and flows through the aperture of the first interface element into the second region, said desolvation means interacts with said matrix material to create reagent ions and to substantially desolvate said pulsed liquid stream into gas phase ions in the second region, and wherein the spacing between the aperture of the capillary tube and the aperture of the first interface element is such that there is minimal expansion of the liquid stream in the first region.

The present invention also provides a number of other features which can be provided either instead of, or in combination with the feature recited in the preceding paragraph (mounting the capillary tube in a manner such that the liquid charge stream flows through into the second region without substantially desolvating). These features include:

(1) locating the outlet of the capillary tube relative to the aperture and dimension of the aperture such that substantially all of the liquid ion current passes through into the second region, whereby only a small or negligible ion current is detected on the first interface element, i.e. a current which is orders of magnitude less than the ion current flowing into the second region;

(2) providing a diameter for the bore of the capillary tube, at the outlet thereof, in the range of 12–125 micrometers, mounting the outlet from the aperture at a distance in the range 50 to 500 micrometers and providing the aperture with a diameter in the range of 5 to 500 micrometers.

(3) mounting the tip of the capillary tube, including the capillary tube outlet, in a cap, the cap including the aperture and the cap serving to locate the outlet of the capillary tube both axially and radially relative to the aperture, wherein the first interface element includes a bore within which the cap is mounted.

(4) while reference has been made to the use of a capillary tube within the ion source apparatus, it should be

understood that instead of using a capillary tube to introduce liquid analyte into the ion source chamber, it would be possible to use any means of introducing a source of liquid analyte into the ion source chamber instead of using a capillary tube.

In a third aspect, the present invention provides a method of forming gas phase ions in a relatively low pressure region from a liquid, the method comprising the steps of:

(a) directing the liquid through a capillary tube having an outlet to provide a liquid stream at a preset flow rate into a first region at a relatively high pressure;

(b) providing an electrode downstream from the aperture;

(c) providing a first interface element including an aperture and separating the first region from a second region at a relatively low pressure;

(d) positioning the capillary tube such that the outlet of the capillary tube is aligned with the aperture of the first interface element and is positioned in front of, and in close proximity to, the aperture of the first interface element;

(e) applying an electric potential between the liquid within said capillary tube and the electrode to form an electric field, sufficient to cause said liquid stream to form a charged liquid stream, whereby the charged liquid stream originates at the outlet of the capillary tube and flows through the aperture of the first interface element into the second region; and

(f) locating the outlet of the capillary tube at a distance from the aperture such that there is minimal expansion of the charged liquid stream in the first region and such that substantially all the liquid passes through the orifice, for vaporization in the second region.

In this third aspect of the invention, it is envisaged that, step (f) and, where applicable step (e), could be replaced or combined with one or more of the following features:

(1) causing substantially all the ion current to pass through the aperture, whereby only a relatively small ion current is detected at the interface element;

(2) spacing the outlet of the capillary tube in the range 50 to 500 micrometers from the aperture, and/or providing the outlet of the capillary tube with a diameter in the range of 12 to 125 micrometers, and/or providing the aperture with a diameter in the range of 5 to 500 micrometers;

(3) locating the aperture such that the jet region of the Taylor cone extends through the aperture, or locating the aperture such that at least a portion of the plume region is located in the aperture and may extend, at least partially, into the first region; and

(4) causing at least 90% of the sample to pass through the aperture into the second region.

In a fourth aspect, the present invention provides a method of forming gas phase ions in a relatively low pressure region from a liquid containing a matrix material, the method comprising the steps of:

(a) directing the liquid through a capillary tube having an outlet to provide a liquid stream at a preset flow rate into a first region at a relatively high pressure;

(b) providing a first interface element including an aperture and separating the first region from a second region at a relatively low pressure;

(c) positioning the capillary tube such that the outlet of the capillary tube is aligned with the aperture of the first interface element and is positioned in front of, and in close proximity to, the aperture of the first interface element;

(d) applying pressure pulses to the capillary tube to cause said capillary tube to expel a series of liquid charge stream droplets to cause the liquid stream flowing through the aperture of the capillary tube to become a pulsed liquid stream that originates at the aperture of the capillary tube and flows through the aperture of the first interface element into the second region;

(e) locating the outlet of the capillary tube at a distance from the aperture such that there is minimal expansion of the charged liquid stream in the first region and such that substantially all the liquid passes through the aperture, for vaporization in the second region; and

(f) desolvating said droplets into gas phase ions in the second region.

Further objects and advantages of the invention will appear from the following description, taken together with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

FIG. 1 is a diagrammatic view of an embodiment of the present invention;

FIG. 2 is a more detailed diagrammatic view of the capillary tube, the liquid charge stream and the first interface element lens of FIG. 1;

FIG. 3 is a more detailed view of the capillary tube of FIG. 1 in association with an interface element barrier;

FIG. 4 is a diagrammatic cross-sectional view of the capillary tube of FIG. 1 in association with an interface element cap;

FIG. 5a is a diagrammatic view of heating equipment for heating the liquid within the capillary tube of FIG. 1;

FIG. 5b is a diagrammatic view of alternative heating equipment for heating the liquid within the capillary tube of FIG. 1;

FIG. 6 is a diagrammatic view of the ion source apparatus of FIG. 1 in association with a microwave generator; and

FIG. 7 is a diagrammatic view of a further embodiment of the present invention utilizing ion spray.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Reference is first made to FIGS. 1 and 2, which show a high intensity ion source apparatus 10 according to a preferred embodiment of the present invention. Ion source apparatus 10 contains an ion source chamber 12 and a vacuum chamber 14.

Ion source chamber 12 contains a capillary tube 16 positioned in front of a first interface element or lens 18 which separates ion source chamber 12 from vacuum chamber 14. First interface element or lens 18 includes an aperture 26. The capillary tube 16 receives liquid analyte (e.g. for test purposes, a small flow of Minoxidil or Reserpine dissolved in solvents such as methanol, acetonitrile, and the like) from an analyte source 22 which may be any appropriate source of liquid analyte, such as a small container of analyte, or eluent from a liquid chromatograph or capillary electrophoresis instrument. Voltage supplies 20 and 21 are connected to capillary tube 16 (and hence to the liquid within) and lens 18, respectively. In order to provide a high electric field at capillary tip 34 (FIG. 2), these voltage supplies are adjusted to provide a high voltage potential difference, typically between 500 and 1600 volts (e.g. 1300 volts).

After charging the liquid at the capillary tube outlet 38, the high electric field applied to capillary tube 16 pulls the charged liquid from capillary tube 16 to produce a liquid charge stream 23 which subsequently disperses into a cloud of charged droplets, according to the well known method of electrospray. Upon evaporation of the charged droplets, gas phase ions are formed. The various physical and electrical characteristics associated with liquid charge stream 23 will be further described in relation to FIG. 2.

Gas source 30a maintains ion source chamber 12 at a pressure of between 10^5 pascals (i.e. atmospheric pressure) and 2×10^5 pascals (i.e. 2 atmospheres). As the pressure is increased above atmosphere (e.g. to 1.5 atmospheres), the possibility of arcing between capillary tip 34 and lens 18 is reduced. At 1.5 atmospheres, 50 percent more gas accompanies liquid charge stream 23 in ion source chamber 12 than would be the case at atmospheric pressure. This increase in gas load is practically acceptable in view of the operational benefits as will be discussed. Gas source 30a is typically N_2, but can also be air.

Vacuum chamber 14 comprises a first vacuum chamber 14a and a second vacuum chamber 14b. The lens 18 of first vacuum chamber 14a contains aperture 26 which is sized to completely receive the Taylor cone of the liquid charge stream 23. Second vacuum chamber 14b houses a mass spectrometer 24 which can be any kind of mass spectrometer, such as an ion trap, a time-of-flight mass spectrometer, or a quadrupole mass spectrometer. By way of example, FIG. 1 depicts first and second vacuum chambers 14a and 14b and shows the positioning of quadrupole rods of a conventional tandem mass spectrometer of the kind which includes an entrance rod set Q0, a first resolving rod set Q1, a second rod set Q2, a fragment ion resolving rod set Q3, and an ion detector 28.

First vacuum chamber 14a (i.e. regions of containment and desolvation) may be maintained at a pressure of approximately 25 pascals by pump 30b. Second vacuum chamber 14b (i.e. for containing the mass spectrometer) may be maintained at a pressure on the order of 10–2 pascals using pump 30c. Typically, the second vacuum chamber 14b (i.e. containing the mass spectrometer) is maintained at a pressure which is appropriate to the type of mass spectrometer. For example, as is conventionally known, quadrapole rod sets for mass analysis need to be maintained at approximately 1.33 millipascals, whereas ion traps should be maintained at approximately 133 millipascals.

FIG. 2 is a more detailed drawing showing the physical geometry of liquid charge stream 23 as discharged by capillary tube 16 (not to scale). The outside diameter of capillary tube 16 tapers from a body 32 to a tip 34 such that tip 34 has a relatively smaller diameter than that of body 32. Capillary tube 16 has a capillary bore 36 formed throughout, such that liquid analyte from the analyte source 22 flows therein. Capillary bore 36 terminates in an outlet 38 formed in tip 34 thereof, from which the liquid charge stream 23 emanates. Capillary tube 16 can be made of any suitable material, such as steel, conducting polymers, fused silica, and glass (e.g. soda lime glass, borosilicate glass). Tips 34 constructed of fused silica or glass are often metallized with a material such as gold, silver, or platinum by processes such as sputtering or vapour deposition.

The characteristic geometry of the electrospray liquid charge stream, conventionally called a Taylor cone, is formed when liquid charge stream 23 emerges from capillary tube 16 at high electrical field. The liquid charge stream 23 accelerates towards lens 18 and assumes the character-

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istic conical geometry (Region A). At the apex of the cone, a high velocity jet emerges (Region B) which subsequently breaks into highly charged droplets (Region C). As will be further described, the highly charged droplets in Region C are generally evaporated with dry gas or heat to produce rapid droplet desolvation and formation of gas phase ions. In effect, the electric field pulls liquid charge stream 23 from capillary tube 16 to produce a cloud of charged droplets so that upon evaporation, gas phase ions will be formed. While it is desirable to adjust the system parameters of ion source apparatus 10 such that Region C of the Taylor cone is completely positioned within first vacuum chamber 14a, it should be understood that it would also be beneficial to adjust system parameters such that a lesser portion of Region C is provided to vacuum chamber 14a, i.e. so an initial portion of Region C is within the ion source chamber 12, as long as substantial desolvation of liquid charge stream 23 can be still be said to occur within vacuum chamber 14a. The extent to which Region C can commence in, or be partially located in, the first vacuum chamber 14a will depend on the size of the aperture 26 and the extent to which one can tolerate a loss of sample due to impingement of the periphery of the expanding Region C on the interface element or lens 18.

For conductive capillaries, tip 34 should be of conical shape where liquid charge stream 23 emerges, so that a single Taylor cone liquid charge stream 23 is emitted from outlet 38. For example, a flat tip on capillary tube 16 tends to produce an unstable Taylor cone liquid charge stream 23 because the electric field concentrates on the outer edges. Accordingly, the diameter of body 32, which is greater than the diameter of tip 34, tapers from the body 32 to the tip 34 to form a uniform conical section.

The outer diameter of body 32 is preferably 180 micrometers but can have any reasonable dimension. The inner diameter of bore 36 is preferably 50 micrometers to accommodate a flow rate of between 0.5 microliters per minute and 5 microliters per minute but may range anywhere from between 12 micrometers and 125 micrometers. Outlet 38 of capillary tube 16 is positioned from aperture 26 of lens 18 at a distance of between 50 micrometers and 500 micrometers, and preferably at 250 micrometers (recognizing that the lens 18 can have a significant thickness, this distance is measured from the face of the lens 18 bounding the chamber 12). It should be noted that it has been experimentally determined that it is beneficial to adjust the distance between the capillary tip 34 and the aperture 26 of lens 18 such that it is less than 10 times the length of the Taylor cone.

For nonconductive capillaries, the shape of the capillary tip is of less significance, but a conical shape is preferred, so that the emerging liquid tends to form a single Taylor cone.

Lens 18 has aperture 26 with a diameter of between 5 and 500 micrometers, and preferably a diameter of approximately 50 micrometers. As previously described, the lens aperture diameter is sized appropriate to the diameter of the Taylor cone. The diameter of aperture 26 will be larger than the Taylor cone ion stream "waist", or the minimum diameter of charge liquid stream 23. As the diameter of aperture 26 is made smaller, the gas load from ion source chamber 12 to first vacuum chamber 14a is decreased, thereby reducing the pumping speed and cost of vacuum pump 30b. The alignment of liquid charge stream 23 passing through outlet 38 with aperture 26 is performed using an adjuster 42a (shown in FIG. 1), as is conventionally known.

As described above, system parameters, including the spacing of capillary tip 34 from lens 18 must be such that the Taylor cone extends into vacuum chamber 14 and that substantial desolvation of liquid charge stream 23 occurs within vacuum chamber 14a. According to this technique, liquid ions and solvent droplets are provided to the low pressure region of first vacuum chamber 14a from the high pressure region of ion source chamber 12, with minimal desolvation occurring within ion source chamber 12. Specifically, the length of the Taylor cone is dependent on the liquid flow rate, the liquid surface tension and charge density of the liquid. Surface tension of the liquid depends on the type and temperature of the liquid, and the pressure of the surrounding gas. Charge density of the liquid depends on the composition of the liquid, and on the amount of electric field applied at capillary tip 34.

Liquid charge stream 23 is pumped through capillary tube 16 at generally a constant rate of flow by the pump associated with analyte source 22 (not shown). While a maximum flow rate of 2 microliters per minute is preferred, other flow rates up to about 5 microliters per minute can be accommodated. For an orifice diameter of 25 to 50 micrometers, it is preferred that voltage sources 20 an 21 provide a potential difference between capillary tube 16 and lens 18 of between 500 volts and 1600 volts.

As shown in FIG. 2, the large electric field at capillary tip 34 not only causes charge separation in the tip, it also causes the resulting charged liquid flow velocity to increase as the liquid leaves the capillary tip 34. Due to conservation of mass and the high incompressibility of liquids, as the flow velocity increases, the diameter of the liquid stream decreases as shown. Eventually the mutual repulsion of the contained charges overcomes the liquid surface tension, at which point the liquid stream disperses into a series of charged droplets inside the vacuum chamber 14a, as shown.

Referring back to FIGS. 1 and 2, and using the system dimensions and parameters listed in the following table, the Taylor cone of liquid charge stream 23 has been observed to pass through aperture 26 into the vacuum chamber 14 before breaking down into charged droplets, resulting in substantially increased ion current, and decreased gas load due to the much smaller aperture 26 that can be used.

Parameter	Approximate Value	Parameter	Approximate Value
diameter of body 32	117 micrometers	ion source vacuum chamber pressure	10^5 pascals
diameter of bore 36 (and outlet 38)	50 micrometers	first vacuum chamber pressure	13 pascals
diameter of aperture 26	50 micrometers	voltage applied between capillary 16 and lens 18	1300 volts
distance between outlet 38 and aperture 26	250 micrometers		

Specifically, standard solutions, Minoxidil and Reserpine, were each provided at a concentration of about 100 picograms per microliter at a flow rate of 2 microliters per minute and electrosprayed within ion source apparatus 10 having the above noted system dimensions and parameters. When these solutions were electrosprayed from atmosphere through aperture 26 into first vacuum chamber 14a at a pressure of 13 pascals, the Q0 rod set, used as a Faraday cup for measuring the ion current, measured ion currents of 80×10^{-9} amperes and 100×10^{-9} amperes, respectively. In contrast, ion currents produced under typical electrospray or ion spray conditions are approximately 2.5×10^{-10} amperes.

Accordingly, ion current increases of 300 to 400 times can be achieved. When outlet 38 is properly aligned with aperture 26, no significant ion current is detectable on the lens 18, i.e., less than one percent of the maximum, which is indicative of negligible losses due to any of the Taylor cone striking lens 18. The ion/gas ratio for the experimental setup described above was determined to be 1 ion per 10^7 molecules, a 1000 fold increase over typical ion source systems.

With a relatively small vacuum pump, namely a 50 l/s vacuum pump for pump 30b (FIG. 1), upon turning on the liquid analyte flow, a five percent pressure increase in vacuum chamber 14a was observed from 1.04 to 1.09 pascals using an aperture 26 of 50 micrometers. Therefore solvent pressure increases were observed to be relatively minor compared with the gas flow from ion source chamber 12. If first vacuum chamber 14a is maintained at a higher pressure, such as 133 pascals, the pumping demand is lowered and accordingly a less expensive pump 30b can be used.

It is not necessary to use voltage supply 20 to apply a voltage differential across capillary tube 16 and first interface element lens 18. Specifically, as shown in FIG. 3, a nonconductive interface element "barrier" 19 and a counter-electrode 39 comprising the Q0 assembly, maintained at an appropriate potential by voltage supply 20, positioned downstream from the interface element barrier 19, can be used in place of the conductive lens 18 discussed above. It should be understood that any conductive element may form the counter-electrode 39.

Specifically, an ESI source having a flow rate of approximately 2 microliters per minute with a capillary tip 38 is shown approximately 0.125 millimeters away from an aperture 27 in nonconductive interface element barrier 19. Interface element barrier 19 has an aperture diameter of approximately 50 micrometers. When counter-electrode 39, is placed approximately 15 millimeters downstream of the capillary tip, a Taylor cone ion charge stream 23 is produced that does not disperse into droplets until it enters first vacuum chamber 14a.

Conventional electrospray conditions are provided to the apparatus, i.e., the flow rate is approximately 2 microliters per minute and approximately 5000 volts is applied between the capillary and downstream counter-electrode 39. It should be noted that aperture 27 of nonconductive interface element barrier 19, positioned about the Taylor cone ion charge stream 23, maintains the pressure differential between the atmospheric and vacuum regions. This configuration is advantageous in the case where the length of the Taylor cone is variable due to changes in the composition of the liquid, as is the case with a liquid chromatograph (gradient run) having different operational modes. This design is also much less susceptible to electrical breakdown due to mechanical or electrical misadjustment. One possible disadvantage could be the occurrence of surface charging of the interface element barrier 19 but this could be avoided by making appropriate adjustments to system conditions, such as increasing the diameter of aperture 27 (e.g. 150 micrometers). Although increasing the diameter of aperture 27 will increase the gas flow necessitating a larger vacuum pump, this will result in a higher tolerance of alignment between capillary bore 36 and aperture 27.

FIG. 4 shows one way of simplifying the task of aligning capillary outlet 38 with either aperture 26 of lens 18 of FIG. 2 or aperture 27 of barrier 19 of FIG. 3. As shown, a generally cylindrical interface cap 18a is provided which fits

over capillary tip 34 and into the lens 18 or barrier 19, with the lens 18 indicated at 18b in FIG. 4. The capillary tube 16 is adapted to fit within the cylindrically symmetric cap 18a, with the capillary tube 16 being separated from cap 18a by a section of insulator 33. A shoulder 31 on capillary tube 16 locates capillary tube 16 and surrounding insulation 33, axially within cap 18a.

Cap 18a is secured in place in a suitably dimensioned opening in a lens support 18b of lens 18. Again, a shoulder 41 on lens cap 18a abuts a shoulder of the lens 18b and locates the cap 18a axially within lens support 18b and hence locates the entire assembly within lens 18. An "O" ring 35 around the cap 18a prevents gas leakage from ion source chamber 12 into the first vacuum chamber 14a. Holes 37a in cap 18a maintain the pressure in a tip chamber 37 at substantially the same pressure as chamber 12, here atmospheric pressure. The tip chamber 37 is defined by the end of the capillary 16 and the cap 18a, and the Taylor cone. The aperture 26 is now provided in the cap 18a and this liquid charge stream 23 assembly allows for the accurate and stable alignment of capillary bore 36 with aperture 26 of cap 18a, such that a fixed distance between capillary tip 34 and aperture 26 can be maintained.

Referring back to FIG. 1, as liquid charge stream 23 enters into vacuum chamber 14 through aperture 26, the desolvation of liquid charge stream 23 can be greatly assisted by use of a laser 44 having a beam directed at the emerging liquid charge stream 23 as shown. Laser 44 can be any appropriately powered laser, such as the model 48-5, Duo-Lase 50 W continuous infrared laser (10.6 micrometers). The laser beam of laser 44 is appropriately focused onto liquid charge stream 23 as it enters vacuum chamber 14 through aperture 26. For certain applications it may be more appropriate to use a pulsed laser. Due to the high liquid velocity at the end of the Taylor cone of liquid charge stream 23, the laser repetition rate would be in the kilocycle range for maximum efficiency.

It will be appreciated that, in principle, any source of electromagnetic radiation can be provided which has a wavelength that is absorbed by the liquid, and for this purpose the liquid can include substances to increase the adsorption of radiation. Other light sources could be used, or a microwave source as detailed below. The beam from such a source can be arranged to intersect the Taylor cone charge stream 23 at an angle, or it could be more or less axially aligned with the charge stream.

The relative position of the output beam of laser 44 with respect to liquid charge stream 23 can be adjusted using the micrometer screws of adjusters 42a and 42b to adjust the position of the capillary tube 16 and the laser, respectively, as is conventionally known. It should be noted that laser 44 could also be located within ion source vacuum chamber 12 such that the laser beam is focused on liquid charge stream 23 in close proximity to aperture 26. It would be necessary to ensure that the diameter and the power of the laser beam of laser 44 does not cause excessive radial expansion of liquid charge stream 23 beyond the dimensions of aperture 26, i.e., to prevent significant amounts of ion current from appearing on the lens 18.

It should be understood that it would also be possible to combine a "matrix" material with the analyte liquid in solution as a variation of the well known matrix assisted laser desorption ionization (MALDI) to ionize the analyte by fast ion-analyte reactions, although here the "matrix" must permit a solution to be formed rather than a solid. Essentially, the "matrix" material is selected to absorb

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energy from the laser beam for the express purpose of creating reagent ions. The liquid in this instance is usually not charged, i.e., there is no large electric field at the capillary tip. In addition to creating reagent ions via the matrix, the laser energy also desolvates the liquid. It should be understood that the matrix actually promotes ionization as it surrounds the large analyte molecules so that the fast laser energy creates intact gas phase analyte molecules which are subsequently ionized by collisions with reagent ions. It should also be understood that by attaching a conventionally known piezoelectric device 17 (FIG. 1) to capillary body 32, pressure pulses can be applied to the liquid within capillary tube 16 of FIG. 1. In this way, capillary tube 16 may act as a single droplet generator, whose pulse frequency can be synchronized with that of a pulse laser.

Still referring to FIG. 1, upon entering vacuum chamber 14, the ions are focussed by appropriate potentials on the AC-only rod set Q0 and guided from first vacuum chamber 14a through the interchamber aperture 48 in a second interface lens 49 into second vacuum chamber 14b containing rod set Q1. An AC RF voltage (typically at a frequency of about 1 MHz) is applied between the rods of rod set Q0, as is well known, to permit rod set Q0 to perform its guiding and focusing function. Both DC and AC RF voltages are applied between the rods of rod set Q1 so that rod set Q1 performs its normal function as a mass filter, allowing only ions of selected mass to charge ratio to pass through to the second rod set Q2 for detection by ion detector 28.

In known manner, if rod set Q2 is enclosed and configured as a collision cell, the precursor ions, selected by rod set Q1, can be fragmented by rod set Q2 and further mass analyzed by rod set Q3. This gives a known MS/MS result.

As previously discussed, reasonably low pressures must be maintained in first and second vacuum chambers 14a and 14b to ensure the proper transmission of ions through vacuum chamber 14. If the pressure within vacuum chamber 14 is increased outside the preferred range, ion signal and/or resolution falls off substantially.

For certain applications, it is useful to maintain the temperature of liquid charge stream 23 as high as practical possible, to increase desolvation of the droplets that are eventually formed in vacuum chamber 14a. Increasing the temperature of the ion charge stream 23 can be achieved by applying heat to the capillary tube 16 to heat the liquid inside. The liquid inside capillary tube 16 can be heated using piezoelectric heating, microwave heating, ultrasonic heating, and infrared heating.

FIG. 5a shows the conventionally known method of heating the liquid flowing through capillary tube 16 by heating capillary tube 16 by heating ion source chamber 12, as shown by band heater 64. The pressure and composition of gas(es) within ion source chamber 12 are controlled by a gas manifold (not shown).

Gas source 30a is used to provide a gas (e.g. N_2) to maintain ion source chamber 12 at a pressure of between 10^5 pascals (i.e. atmospheric pressure) to 2×10^5 pascals (i.e. two atmospheres). Gas source 30a is typically N_2, but other gases which are more effective at suppressing discharges or heat transfer characteristics can also be used. Pressures over atmosphere also act to suppress discharges, especially in the case where negative ions are being generated. Using this configuration, first vacuum chamber 14a can be maintained at a relatively low pressure of approximately 25 pascals.

FIG. 5b shows an alternative method of heating the liquid in capillary tube 16, as described in U.S. Pat. No. 4,935,624,

the contents of which are hereby incorporated by reference. Capillary tube 16 is enclosed within a heater tube 50 and heated directly by a low voltage high current power supply 52 using a feedback controller 54 to regulate power supply 52. As shown, the temperature of heater tube 50 is controlled by thermocouple 56. This method of capillary heating is more controllable than the heating method described in relation to FIG. 5a.

Ion source chamber 12 can also be provided with heated gas by coupling a heating element to the gas delivery tube of gas source 30a, shown coupled to ion source chamber 12 in FIG. 1. Specifically, this can be accomplished using a conventional stainless steel tube (not shown) with appropriate dimensions (e.g. having a diameter of approximately 3.17 millimeters) wrapped around a cylindrical heater (not shown) such that the tip of the tubing expels hot N_2 gas directly at capillary tip 34. This approach ensures that clean gas accompanies the liquid charge stream 23 into first chamber 14a, and that capillary tip 34, and thus the liquid flowing through it, is heated.

Heat may also be applied to first vacuum chamber 14a using heating tape 47 (e.g. such as Fisher Cat. No. 11-463-22° C. type tape) wrapped around the outside of first vacuum chamber 14a in association with a power supply 46, as shown in FIG. 1. It should be understood that is also possible to provide heat to the system by heating the Q0 rods directly or other assemblies within vacuum chamber 14 which can assist droplet desolvation using such phenonemon as black body radiation and heating of residual gases. It should also be noted that by heating these components, deleterious contamination effects can also be avoided.

While it is desirable to use heating methods as discussed above to desolvate the Taylor cone of the liquid charge stream 23, it should be understood that if too much heat is applied to capillary tube 16, not all of liquid charge stream 23 will pass through aperture 26 in lens 18. As heat is applied, the droplet surface tension of the liquid is reduced and the liquid charge density will be able to overcome the surface tension sooner which reduces the length of the Taylor cone of liquid charge stream 23. This increases the possibility that ions will strike lens 18. Further, when added heat causes the liquid to boil, gas bubbles will disrupt the shape of the liquid at the capillary tip, causing unstable charging of the Taylor cone of liquid charge stream 23.

FIG. 6 shows an alternative liquid charge heating technique, namely a microwave generator 72 configured within ion source apparatus 10 for heating and thus, for promoting the desolvation of the liquid droplets from the Taylor cone of liquid charge stream 23. This configuration provides a standing wave of energy at the entrance to the first vacuum chamber 14a, the energy of which causes desolvation of the liquid droplets of the Taylor cone of the liquid charge stream 23, preferably in the vicinity of the entrance rod set Q0. It should be understood that other methods of conventionally known liquid droplet desolvation could be used in conjunction with the microwave heating method described above.

It should be understood that many different conventionally known ion transport and containment techniques may also be used within the present apparatus. One particularly noteworthy containment mechanism for directing ions into mass spectrometer 24 is the well known ion funnel 92 as shown in FIG. 6 and as described in "A Novel Ion Funnel for Focusing Ions at Elevated Pressures using Electrospray Ion Mass Spectrometry" by Richard Smith et al., Rapid Comm. Mass Spec. 11, 1813–1817 (1997). It has been experimen-

tally determined that maximum efficiency results when ion funnel 92 is operated at about 130 pascals.

It should also be also understood that where the sample flow rate exceeds approximately 5 microliters per minute, the flow from analyte source 22 (FIG. 1) must be reduced to this maximum in order to conform to the ESI conditions of a single Taylor cone. Often, this is not convenient, and it is easier to adapt an ion spray source to accommodate high flow rates so that it delivers substantially liquid ion current to the first vacuum region 14a, as shown in FIG. 7. Liquid sample flows through a bore 74 of an ion source capillary 76 and emerges from a capillary tip 77. A voltage difference between the liquid in the capillary 76 and the cone-shaped lens 18 typically creates multiple Taylor cones of the liquid from the capillary tip outer edge 79 (shown schematically). High speed gas flowing axially between a nebulizer tube 78 and capillary 76, reduces the size of the larger charged droplets. The capillary tip 77 is placed close enough to the aperture 26 of lens 18 to ensure that a significant ion current of substantially liquid form flows through aperture 26. The high speed nebulizer gas assists in transporting charged liquid quickly towards the aperture 26, while the cone shape of lens 18 allows for a smooth flow of the nebulizer gas over the surface of lens 18. In FIG. 7, aperture 26 is sized to have a diameter of approximately 250 micrometers, the distance between the capillary tip 77 and the lens aperture 26 is approximately 1 millimeter and the diameter of the capillary bore 74 is typically greater than 100 micrometers. Although a single on-axis ion spray capillary 76 and nebulizer tube 78 are shown, multiple simultaneous sprayers could easily be configured for use. An ion spray could have a high flow rate of, for example, 200 microliters per minute. At this flow rate, it is only necessary for a small fraction, for example, 5% to pass through the aperture 26, and this will still give an adequate ion current.

Although the use of first vacuum chamber 14a as the only intermediate chamber between ion source chamber 12 (at substantially atmospheric pressure) and second vacuum chamber 14b (at pressures necessary for satisfactory mass spectral performance) has been described, it should be understood that a series of said chambers, each having successively lower pressures, could be used in place of first vacuum chamber 14a. Further, each chamber could be provided with one or more aforementioned containment mechanisms. Also, although entrance rod set Q0 in vacuum chamber 14a has been described as quadrupolar it should be understood that multipolar configurations such as hexapole or octopole are possible. In addition, techniques to create an axial field using ion containment such as the apparatus described in U.S. Pat. No. 5,847,386, could also be applied to ion source apparatus 10.

By appropriately selecting a particular set of capillary dimensions, lens or barrier apertures, capillary to counter-electrode voltage and spacing, capillary to lens or barrier spacing, surrounding pressure and heat, an appropriate combination of desolvation devices, an appropriate combination of vacuum chambers for desolvation and ion transport, the present invention provides the advantages of improved flow of ions into vacuum from an electrospray source such that a low volume of gas is admitted into the vacuum chamber along with the ions, such that corona effects are avoided, such that boiling does not occur, and such that the lab footprint of requisite pumping equipment is reduced.

The lens 18 or barrier 19 have been described as separating an atmospheric pressure region from a vacuum region, and it has been noted that the pressure in chamber 12 could be up to 266 pascals (i.e. 2 atmospheres). However, in general terms, the essential concept is to maintain the outlet of capillary tube 16 in a relatively high pressure environment. The gas pressure surrounding capillary tube 16 needs to be high enough to prevent premature boiling of the solvent, so that a stable Taylor cone is formed. The gas pressure also needs to be high enough to prevent corona discharge (very low pressures can prevent corona discharge, but are unacceptable on the boiling criterium just mentioned). The capillary outlet is placed close enough to an aperture in a lens or the like, such that the Taylor cone extends through the aperture into a second lower pressure chamber, before it substantially disperses or breaks down into charged droplets. The pressure in the low pressure chamber will in general depend upon the requirements of other elements housed by the low pressure chamber. For example, if quadrupole rod sets or other ion focussing devices are used in the low pressure chamber, their characteristics will determine a desired pressure in the low pressure chamber.

Thus, the technique of the present invention provides the advantages of discharging the electrospray into a high pressure region, while enabling all, or substantially all, of the electrospray stream to be transferred into a low pressure region, where the ions can be desolvated, collected and focussed. This is expected to give a very high level of efficiency for ion generation and much reduced ion loss. Additionally, only a small aperture is required between the two pressure regions, thus considerably reducing the pumping requirements in the low pressure region.

It will be appreciated that the ion source or gas phase ions of the present invention can be supplied to any suitable ion mobility separator downstream of first vacuum chamber 14a, possibly for application to any suitable spectrometer, including tandem mass spectrometers, time of flight (TOF) spectrometers, and in general any mass analyzer or mass spectrometer requiring desolvated ions in a very low pressure environment.

As will be apparent to persons skilled in the art, various modifications and adaptations of the structure described above are possible without departure from the present invention, the scope of which is defined in the appended claims.

What is claimed is:

1. An apparatus for providing gas phase ions in a relatively low pressure region from a liquid, the apparatus comprising:

(a) a capillary tube, said capillary tube having an input for receiving the liquid, a longitudinal bore, and an outlet for discharging said liquid at a preset flow rate into a first region at a relatively high pressure;

(b) a first interface element with an aperture therein and separating said first region from a second region at a relatively low pressure;

(c) an electrode located downstream from the outlet of the capillary tube; and

(d) a voltage source for generating a voltage potential between said liquid in the capillary tube and said electrode;

wherein the outlet of the capillary tube is aligned with the aperture of the first interface element and is positioned directly in front of, and in close proximity to the aperture of the first interface element, whereby, in use, with a sufficient voltage potential applied between the liquid and the electrode to form an electric field sufficient to cause the liquid stream flowing through the outlet of the capillary tube at the preset flow rate to become a liquid stream in the form of a

Taylor cone having a jet region that originates at the outlet of the capillary tube and flows through the aperture of the first interface element into the second region and substantially desolvates into gas phase ions in the second region, and wherein the spacing between the outlet of the capillary tube and the aperture of the first interface element is such that the jet region of the Taylor cone is positioned within the aperture of the first interface element so that the liquid stream disperses into charged droplets substantially in the second region.

2. An apparatus as claimed in claim 1, which includes heating means for supplying energy to droplets in the second region to promote vaporization.

3. An apparatus as claimed in claim 2, wherein the heating means comprises a laser mounted such that the beam from the laser intersects the liquid stream as it emerges into the second region through the aperture of the first interface element.

4. An apparatus as claimed in claim 2, which further comprises a first chamber defining the first region with the capillary tube located in the first chamber, second chamber defining the second region, and wherein the heating means includes means for heating the second chamber.

5. An apparatus as claimed in claim 4, wherein the heating means comprises at least one of: means for supplying gas to the second chamber and for heating the gas; a laser for irradiating the droplets to heat said droplets; a microwave generation means for heating droplets with microwave energy; an infrared heater for heating said droplets with infrared heat; and a heater including a length of heating tape wrapped around the outside of the second chamber to provide thermal heat to said droplets.

6. An apparatus as claimed in claim 5, which additionally includes means for heating the capillary tube, to promote vaporization of droplets.

7. An apparatus as claimed in claim 4, which includes an ion guide in the second chamber for collecting and guiding ions.

8. An apparatus as claimed in claim 4, which includes a third chamber and pump means for evacuating the second and third chambers to a sub-atmospheric pressure, a mass spectrometer located in the third chamber, a second interface element separating the second and third chambers, and a further aperture in the second interface element providing communication between the second and third chambers, wherein the apparatus is configured to be operated such that the pressure in the second chamber is less than the pressure in the first region and the pressure in the third chamber is less than the pressure in the second chamber.

9. An apparatus as claimed in claim 1, wherein the diameter of the outlet of the capillary tube is less than or equal to the diameter of the aperture of the first interface element.

10. An apparatus as claimed in claim 1, wherein the diameter of the outlet of the capillary tube is in the range of 12 micrometers and 125 micrometers.

11. An apparatus as claimed in claim 1, wherein the diameter of the aperture of the first interface element is in the range of 5 micrometers to 500 micrometers.

12. An apparatus as claimed in claim 10, wherein the diameter of the aperture of the first interface element is in the range of 5 micrometers to 500 micrometers.

13. An apparatus as claimed in claims 1, 10, 11 or 12, wherein the outlet of the capillary tube is spaced from the aperture of the first interface element by a distance in the range of 50 and 500 micrometers.

14. An apparatus as claimed in claim 1, wherein the voltage source is capable of providing a potential difference

between said capillary tube and said electrode in the range of 500 volts and 1600 volts.

15. An apparatus as claimed in claim 1, wherein a piezoelectric device is coupled to the capillary tube for applying a series of pressure pulses to the liquid within the capillary tube to cause said capillary tube to expel a series of liquid stream droplets.

16. An apparatus as claimed in claim 1, wherein a piezoelectric device is coupled to the capillary tube for applying a series of pressure pulses to the liquid within the capillary tube, the frequency of said series of pressure pulses being synchronized with the frequency of operation of the laser.

17. An apparatus as claimed in claim 3, wherein the laser comprises a solid state laser.

18. An apparatus as claimed in claim 7, wherein the ion guide in the second chamber comprises one of a quadrupole rod set and an ion funnel.

19. An apparatus as claimed in claim 1, wherein the capillary tube is conductive.

20. An apparatus as claimed in claim 1, wherein the first interface element is conductive and wherein said first interface element and said electrode are integral with one another.

21. An apparatus as claimed in claim 1, wherein the first interface element is an insulator.

22. An apparatus as claimed in claim 1, which additionally includes a nebulizer tube axially located around the capillary tube for providing a flow of relatively high speed gas coaxially with the charged liquid stream.

23. An apparatus as claimed in claim 1, wherein the first interface element is provided with a bore, and wherein a cap is provided mounted within the bore and around the capillary tube, to define a tip chamber into which the outlet of the capillary tube opens, the cap including holes providing communication between the tip chamber and the first region and providing the aperture.

24. An apparatus as claimed in claim 23, which includes at least one of: a shoulder on the capillary tube locating the cap axially on the capillary tube, and cooperating shoulders on the cap and the bore of the first interface element, locating the cap within the bore of the first interface element.

25. An apparatus as claimed in claim 24, wherein the cap is formed of electrically conductive material, and wherein an insulator is provided between the cap and the capillary tube.

26. An apparatus as claimed in claim 24 or 25, which includes a seal between the cap and the bore of the first interface element.

27. An apparatus for providing gas phase ions in a relatively low pressure region from a liquid including a matrix material, the apparatus comprising:

(a) a capillary tube, said capillary tube having an input receiving the liquid, a longitudinal bore, and an outlet for discharging said liquid at a preset flow rate into a first region at a relatively high pressure;

(b) pulsing means coupled to the capillary tube for providing a series of pressure pulses to the liquid within the capillary tube to cause said capillary tube to expel a series of liquid stream droplets;

(c) a first interface element with an aperture therein and separating said first region from a second region at a relatively low pressure;

(d) desolvation means for desolvating the liquid stream droplets into gas phase ions in the second region, wherein the outlet of the capillary tube is aligned with the aperture of the first interface element and is positioned directly in front of, and in close proximity to, the aperture of

the first interface element, whereby, in use, when said pulsing means provides sufficient pulsing action to the capillary tube to cause the liquid stream flowing through the outlet of the capillary tube at the preset flow rate to become pulsed liquid stream that originates at the outlet of the capillary tube and flows through the aperture of the first interface element into the second region, said desolvation means interacts with said matrix material to create reagent ions and to substantially desolvate said pulsed liquid stream into gas phase ions in the second region, and wherein the spacing between the outlet of the capillary tube and the aperture of the first interface element is such that the liquid stream issuing from the outlet of the capillary tube is substantially drawn through the aperture of the first interface element into the second region before dispersing into charged droplets in the second region.

28. An apparatus as claimed in claim 27, wherein the pulsing means is a piezoelectric device.

29. An apparatus as claimed in claim 27, wherein the desolvation means comprises a laser for irradiating the droplets to heat said droplets.

30. An apparatus as claimed in claim 27, which includes a third chamber and pump means for evacuating the second and third chambers to a sub-atmospheric pressure, a mass spectrometer located in the third chamber, a second interface element separating the second and third chambers, and a further aperture in the second interface element providing communication between the second and third chambers, wherein the apparatus is configured to be operated such that the pressure in the second chamber is less than the pressure in the first region and the pressure in the third chamber is less than the pressure in the second chamber.

31. An apparatus as claimed in claim 27, wherein the first interface element is conductive.

32. An apparatus as claimed in claim 27, wherein the diameter of the outlet of the capillary tube is less than or equal to the diameter of the aperture of the first interface element.

33. An apparatus as claimed in claim 27, wherein the diameter of the outlet of the capillary tube is in the range of 12 micrometers and 125 micrometers.

34. An apparatus as claimed in claim 27, wherein the diameter of the aperture of the first interface element is in the range of 5 micrometers to 500 micrometers.

35. An apparatus as claimed in claim 33, wherein the diameter of the aperture of the first interface element is in the range of 5 to 500 micrometers.

36. An apparatus as claimed in claim 27, wherein the outlet of the capillary tube is spaced from the aperture of the first interface element by a distance in the range of 50 and 500 micrometers.

37. A method of forming gas phase ions in a relatively low pressure region from a liquid, the method comprising the steps of:

(a) directing the liquid through a capillary tube having an outlet to provide a liquid stream at a preset flow rate into a first region at a relatively high pressure;

(b) providing an electrode downstream from the outlet;

(c) providing a first interface element including an aperture and separating the first region from a second region at a relatively low pressure;

(d) positioning the capillary tube such that the outlet of the capillary tube is aligned with the aperture of the first interface element and is positioned in front of, and inclose proximity to, the aperture of the first interface element;

(e) applying an electric potential between the liquid within said capillary tube and the electrode to form an

electric field sufficient to cause said liquid stream to form a liquid stream in the form of a Taylor cone having a jet region; and

(f) locating the cutlet of the capillary tube at a such a close distance from the aperture such that said jet region of the Taylor cone is positioned within the aperture of the first interface element such that the liquid stream disperses into charged droplets substantially in the second region.

38. A method as claimed in claim 37, wherein the step of applying an electric potential to the liquid within the capillary tube consists of applying the electrical potential between the first interface element and the capillary tube.

39. A method as claimed in claim 37, further comprising heating the droplets in the second region to promote vaporization of the droplets.

40. A method as claimed in claim 37, which includes irradiating the liquid in the second region with electromagnetic radiation, to heat the liquid and promote vaporization of solvent.

41. A method as claimed in claim 40, which includes irradiating the liquid emerging from the aperture into the second region with a laser beam.

42. A method as claimed in claim 39, which includes heating the liquid in the second region by one of: providing a heated gas in the second region; and heating the liquid with microwave energy.

43. A method as claimed in claim 39, which additionally comprises heating the capillary tube, to heat the liquid, thereby to promote vaporization of liquid droplets in the second region.

44. A method as claimed in claim 39, which includes collecting and guiding the ions in the second region in an ion guide.

45. A method as claimed in claim 42, which includes the additional steps of:

(1) focusing the ions with the ion guide;

(2) providing a mass spectrometer and separating the mass spectrometer from the second region with a second interface element plate including a further aperture;

(3) causing the focused ions to pass through the further aperture into the mass spectrometer; and

(4) mass analyzing the ions with the mass spectrometer.

46. A method as claimed in claim 45, which includes maintaining the pressure in the mass spectrometer at a lower pressure than the pressure in the second region.

47. A method of forming gas phase ions in a relatively low pressure region from a liquid containing a matrix material, the method comprising the steps of:

(a) directing the liquid through a capillary tube having an outlet to provide a liquid stream at a preset flow rate into a first region at a relatively high pressure;

(b) providing a first interface element including an aperture and separating the first region from a second region at a relatively low pressure;

(c) positioning the capillary tube such that the outlet of the capillary tube is aligned with the aperture of the first interface element and is positioned in front of, and in close proximity to, the aperture of the first interface element;

(d) applying pressure pulses to the capillary tube to cause said capillary tube to expel a series of liquid charge stream droplets to cause the liquid stream flowing through the outlet of the capillary tube to become a pulsed liquid stream that originates at the outlet of the

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capillary tube and flows through the aperture of the first interface element into the second region;

(e) locating the outlet of the capillary tube at a such a close distance from the aperture such that the liquid charge stream issuing from the outlet of the capillary the is substantially drawn through the aperture of the first interface element into the second region before dispersing into charged droplets in the second region; and

(f) desolvation said droplets into gas phase ions in the second region.

48. A method as claimed in claim **47**, wherein step (f) comprises heating the droplets in the second region to promote vaporization of the droplets.

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49. A method as claimed in claim **47**, wherein step (f) includes irradiating the liquid in the second region with electromagnetic radiation, to heat the liquid and promote vaporization of solvent.

50. A method as claimed in claim **49**, wherein step (f) includes irradiating the liquid emerging from the aperture into the second region with a laser beam.

51. A method as claimed in claim **49**, wherein step (f) includes heating the liquid in the second region by one of: providing a heated gas in the second region; and heating the liquid with microwave energy.

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